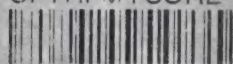
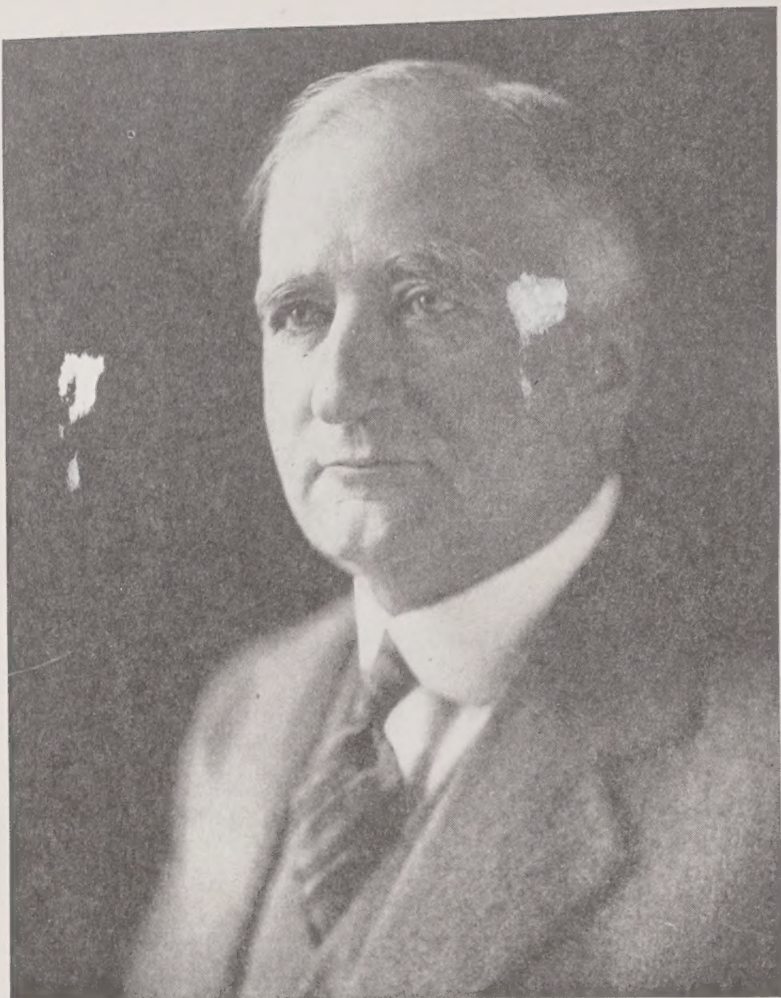


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Industrial chemi.



Dr. Herbert H. Dow (1866-1930), a graduate of Case School of Applied Science (1888), founder of the Dow Chemical Company, and trustee of two learned institutions, provided the country with a never-failing source of bromine and an inexhaustible supply of magnesium.

When just out of college, Dr. Dow founded the Midland Chemical Company (1889), out of which grew the Dow Process Company, which in turn became the Dow Chemical Company (1897). His original purpose was the production of bromine from natural brines by a novel process which required chlorine. The latter substance was produced electrolytically, the bromine successfully extracted, and the numerous investigations started in connection with these products were continued in logical order. At the beginning of the first World War (1914), the Dow Chemical Company found itself one of the most important concerns of its kind in the country. Now, in the throes of a Second World War, the country relies on the company founded by Dr. Dow for two chemical elements essential to the success of the war effort—bromine and magnesium.

INDUSTRIAL CHEMISTRY

AN ELEMENTARY TREATISE FOR THE
STUDENT AND GENERAL READER

BY
EMIL RAYMOND RIEGEL, Ph.D.

PROFESSOR OF INDUSTRIAL CHEMISTRY
UNIVERSITY OF BUFFALO

WITH THE SUPPORT OF A LARGE
NUMBER OF COLLABORATORS



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FOURTH EDITION

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Industrial chemi.

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TO THE CHEMICAL ENGINEERS
AND CHEMISTS OF THE
UNITED NATIONS
WHO ARE
MANUFACTURING THE
MUNITIONS AND WAR MATÉRIEL
ESSENTIAL TO VICTORY
THIS BOOK IS DEDICATED

"Yo te bendigo, Vida
porque veo al final de mi rudo camino
que yo fuí el arquitecto de mi propio destino;
que si extraje las mieles o la hiel de las cosas,
fué porque en ellas puse hiel o mieles sabrosas:
cuando planté rosales, coseché siempre rosas."

AMADO NERVO
(Mexican poet)

Preface to the Fourth Edition

The titanic war which has been forced upon the nation by a treacherous enemy has made the industrial chemist and engineer intent upon only one goal, that of supplying, in the necessary quantities, the goods required for the vigorous prosecution of the war. More than ever has it become evident that the well being, not to say safety, of the nation is linked to the level of its industrial chemical achievements. At the moment, it is to the chemical engineer, seconded by the chemist and able management, that all eyes anxiously turn in the quest for the substitute for Malayan exports; and it is to him that the task of manufacturing 100 octane aircraft fuel in sufficient quantities is assigned. All the members of the relatively small group of chemists and chemical engineers in America know that both these professional missions, and many other less prominent ones, will be successfully and brilliantly discharged.

The last stages of the preparation of the text for the Fourth Edition fell within the war period, yet in spite of increased duties the men consulted have found the time either to tell or write the answers to inquiries, or delegated an associate to do it for them. Not a single project had to be abandoned for lack of replies.

The general scheme of the book is unchanged. Two chapters have been rewritten, those on Paper and Pulp, and on Synthetic Textile Fibers; the chapter on Portland Cement has been brought up to date, which involved a thorough reworking. The chapter on Rubber includes the new developments in synthetic rubbers, as well as the latest advances in working natural rubber. The several innovations in the technology of petroleum called for much space, so that clear and sufficient statements on "aviation gasoline," on alkylation, on the Houdry catalytic process, and on other topics could be made. The bottleneck in our TNT manufacture will not again be toluene, thanks in part to the process of "hydroforming" petroleum fractions.

A number of other changes, smaller in scope, have been made. There have been included: new methods for bleaching and refining sugars, the latest developments in the manufacture and application of dyes, in the hydrolysis of fats, in the distillation of fatty acids. Quiet emphasis has been placed on the manufacture of aluminum metal, and of magnesium metal. The chapter on fuels has been re-examined and re-shaped; a high temperature-high pressure boiler-furnace is included, as well as the result of a long study of the costs of hydroelectric power and of steam power. The chapter on steel has an outline of the processing of a heat, with every test made and every addition recorded, in the basic open hearth. The account of the iron blast furnace operations is fresh from recent observations. Many changes and additions the reader will have to find for himself, small changes in space, yet important ones, all of them. For example, under Radium, radiography is briefly described, for the first time, and a photograph reproduced illus-

trating the results obtainable with a very simple installation. Five new flowsheets are now included, in response to demands by instructors. A number of new illustrations were made available by friends and well-wishers; just as examples of their quality, attention is called to six of them 76, 110b, 138, 148, 192, and 261. All production figures have been brought up to date, with data for the year 1939 or more recent years.

Three new collaborators have contributed their support to the effort to make the present edition an outstanding one. Mr. Harry E. Weston, editorial director of "The Paper Industry and Paper World," wrote the chapter on Paper and Pulp; Mr. Stanley B. Hunt, manager of the Textile Economics Bureau, Inc., N. Y., contributed the main part of the chapter on Synthetic Textile Fibers, as well as its present title; Mr. Ralph H. Wilson, Cataract Chemical Company, Buffalo, whose life is dedicated to the study of leather chemistry, supervised the statement on leather. The contributions of the collaborators in previous editions again lent their support, as acknowledged in the proper places in the text.

My deep thanks are due to numerous managers of governmental agencies for their generous compliance to requests for information, very especially to Mr. T. P. Fitzgerald, Chief Statistician for Manufactures, Bureau of the Census, Department of Commerce, and to his associates; to Mr. Albert R. Merz, Chemist, Bureau of Plant Industry, U. S. Department of Agriculture, who sent intricate figures on nitrogenous materials; and to Mr. O. S. Kiessling, Chief, Basic Materials, Bureau of the Census, for data on Animal and Vegetable Fats and Oils. As far as practicable, separate acknowledgements of other contributions, set at the proper places, have been made in the text. The Minerals Yearbook, published by the Bureau of Mines, supplied a vast amount of information.

Comments and criticisms, favorable or otherwise, are again solicited; a portion of the alterations in the present edition is the result of the advice received from readers.

EMIL RAYMOND RIEGEL

Buffalo, N. Y.,
July 14, 1942.

TABLE OF CHEMICAL AND
ALLIED MANUFACTURES

Table of Chemical and

Relative Importance of Chemical and Allied Manufactures in the United States for the Bureau of the Census, Department of Commerce, supplemented by figures from the

Motor car industry		
Motor vehicles, motor vehicle bodies, parts and accessories	\$4,039,930,733	
Rubber tires and inner tubes	580,928,993	\$4,620,859,726
Iron and steel		
Pig iron (1940)	\$ 827,241,023	
Steel works, rolling mills products	2,720,019,564	3,547,260,587
Petroleum refining		
		2,461,126,549
Leather and leather products		1,389,513,718
Cotton goods		1,168,171,469
Paper	\$ 933,015,664	
and pulp	226,851,822	1,159,866,486
Paints		
	\$ 190,459,858	
and varnishes and lacquers	216,579,605	407,039,463
Cane sugar refining		384,412,492
Druggists' preparations and patent medicines		364,985,404
Glass		357,978,022
Coke and by-products		
		342,197,303
Soap and glycerin		302,634,474
Synthetic organic chemicals not of coal tar origin (1940)		265,307,000
Rayon and allied products		247,065,556
Clay products		240,324,364
Cement, Portland		
		192,611,304
Fertilizers		185,684,328
Cottonseed oil, cake, meal, hulls and linters		171,476,253
Perfumes, cosmetics and other toilet preparations		147,465,585
Beet sugar industry		134,396,017
Corn products; syrup		
	\$ 33,075,823	
corn sugar	13,618,612	
corn oil	12,502,567	
starch (90% from corn)	33,338,359	119,408,253
Dry colors and pigments		83,885,847
Plastic materials, all synthetic resins, casein and others		77,653,314
Dyes (1940)		
	pounds 122,677,000	76,432,000
Explosives		71,053,206
Linseed oil, cake and meal		68,011,767
Compressed and liquefied gases		53,364,936
Mirrors		49,886,406
Gypsum products and building insulation		46,241,980

Allied Manufactures

year 1933, unless otherwise stated; selected and arranged from figures supplied by the United States Tariff Commission, and the Bureau of Mines, Department of the Interior.

Sulfur produced (1941)	50,300,000	
Intermediates for dyes	46,428,219	
Sulfuric acid, made and consumed at the plant	2,496,969 tons	
for sale, value of the	5,152,845 tons	37,880,707
Disinfectants and insecticides, industrial, household, and agricultural (1935)		37,268,449
Lime		36,971,171

Caustic soda, made and consumed at the plant	74,854 tons	
for sale, value of the	950,157 tons	34,541,479
Glue and gelatin		34,331,639
Tanning materials, natural dyestuffs, assistants and sizes (1935)		33,638,800
Soda ash, made and consumed at the plant	815,471 tons	
for sale, value of the	2,146,161 tons	32,871,016
Baking powders, yeast, and other leavening compounds		31,774,637

Ethyl and other alcohols		26,493,208
Salt		24,509,680
Wood distillation and charcoal manufacture		20,957,365
Agricultural insecticides and fungicides (1935)		15,311,231
Boneblack, carbon black and lampblack		14,626,876

Potash salts (1940)		12,562,050
Phosphate rock produced		12,331,662
Bromine (1940)		11,772,515
Chlorine, made and consumed at the plant	172,598 tons	
made for sale, value of the	312,596 tons	10,370,507
Methanol (synthetic)		9,319,752

Medicinals, from coal tar (1940)		7,587,280
Rubber accelerators (1940)		6,370,558
Carbon bisulfide		5,185,708
Butyl alcohol		4,707,910
Hydrochloric acid		3,948,831

Ethyl acetate		3,571,439
Stearic acid		3,550,189
Nitric acid, made and consumed at the plant	133,169 tons	
for sale, value of the	34,571 tons	3,184,912
Oleic acid		3,004,421

WHAT "THINGS CHEMICAL" ARE WORTH:

Average of sales for the year indicated.

Bituminous coal, short ton, f.o.b. mine (1939).....	\$ 1.853
Iron ore, at the mines, long ton (1940)	2.52
Salt, NaCl, short ton (1939)	2.64
Salt in brine (1940)	0.40
Phosphate, Florida land pebble, long ton (1940).....	2.71
Sulfuric acid, 50° Bé., chamber acid, short ton (1941).....	6.75
Lime, chemical and industrial, short ton (1940).....	6.20
Soda ash, short ton (1939)	15.50
Sulfuric acid, 66° Bé., short ton (1941)	16.50
Sulfur, brimstone, long ton (1941)	18.00
Basic pig iron at Valley furnaces, net ton (1940).....	20.00
Sulfite pulp, unbleached, short ton (1939)	33.90
Chlorine, short ton (1939)	33.25
Caustic soda, short ton (1940)	36.40

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When the chemist thinks of the chemical industries he usually places sulfuric acid first. The manufacture of sulfuric acid is par excellence a task for the chemist; in its development, much pioneering, bold for those early days, was done. There will always remain linked to any discussion of sulfuric acid manufacture the fine names of John Glover, Louis Gay-Lussac and George Lunge.

Chapter 1

Sulfuric Acid—Part I: The Chamber Process

Sulfuric acid is manufactured either by the chamber process or by the contact process. In the chamber process the acid made is rather weak, about 70 per cent H_2SO_4 ; the contact process produces 100 per cent acid and stronger grades containing the anhydride SO_3 in excess (the oleums). The chamber process is the older; it is characterized by comparatively large reaction chambers made of sheet lead. In its original form, it represented the leisurely gait of the nineteenth century; it has maintained its place mainly because its product is concentrated enough and pure enough for the manufacture of superphosphate of calcium, a fertilizer. The contact process, on the other hand, produces the strong acid necessary for certain chemical reactions, such as those involved in the manufacture of dye intermediates. This process is characterized by the use of a solid "contact" substance, such as finely divided platinum, vanadium pentoxide, or ferric oxide.

The chamber process has lost ground; there is still a greater number of chamber sets than of contact plants, but the contact plant tonnage passed the chamber set tonnage in 1939.

	1929	1935	1937	1939
Chamber sets	141	71	98	95
Contact plants	42	63	70	70

In production, chamber acid has fallen behind:

Chamber acid 1939	3,411,007 tons 50° Bé. 44.5% of total
Contact acid 1939	4,238,807 tons 50° Bé. 55.5% of total

The contact acid has gained steadily; in 1921, it was 25.2% of the total tonnage; in 1923, 27.6; in 1925, 29.2; in 1929, 36.2; in 1935, 47.2; in 1937, 48.9; in 1939, it passed 50%, reaching 55.5%. The trend is due to the development of extremely compact installations for manufacturing sulfuric acid with vanadium masses, and to the standardization of such plants. This development in turn has been favored by the availability of brimstone at reasonable prices. Another reason for the greater growth of the contact process is that by it, acid of any strength, including the oleums, may be prepared with no other difficulty than diluting for the lower strengths; whereas by the chamber process, acid stronger than 55° Bé. can be made only by an additional operation, and oleums cannot be prepared at all. The trend, however, will be less pronounced in the coming years because of the ingenious advances in chamber construction and operation, described under Modern Developments. In the operation of chamber plants, the potting of nitre is

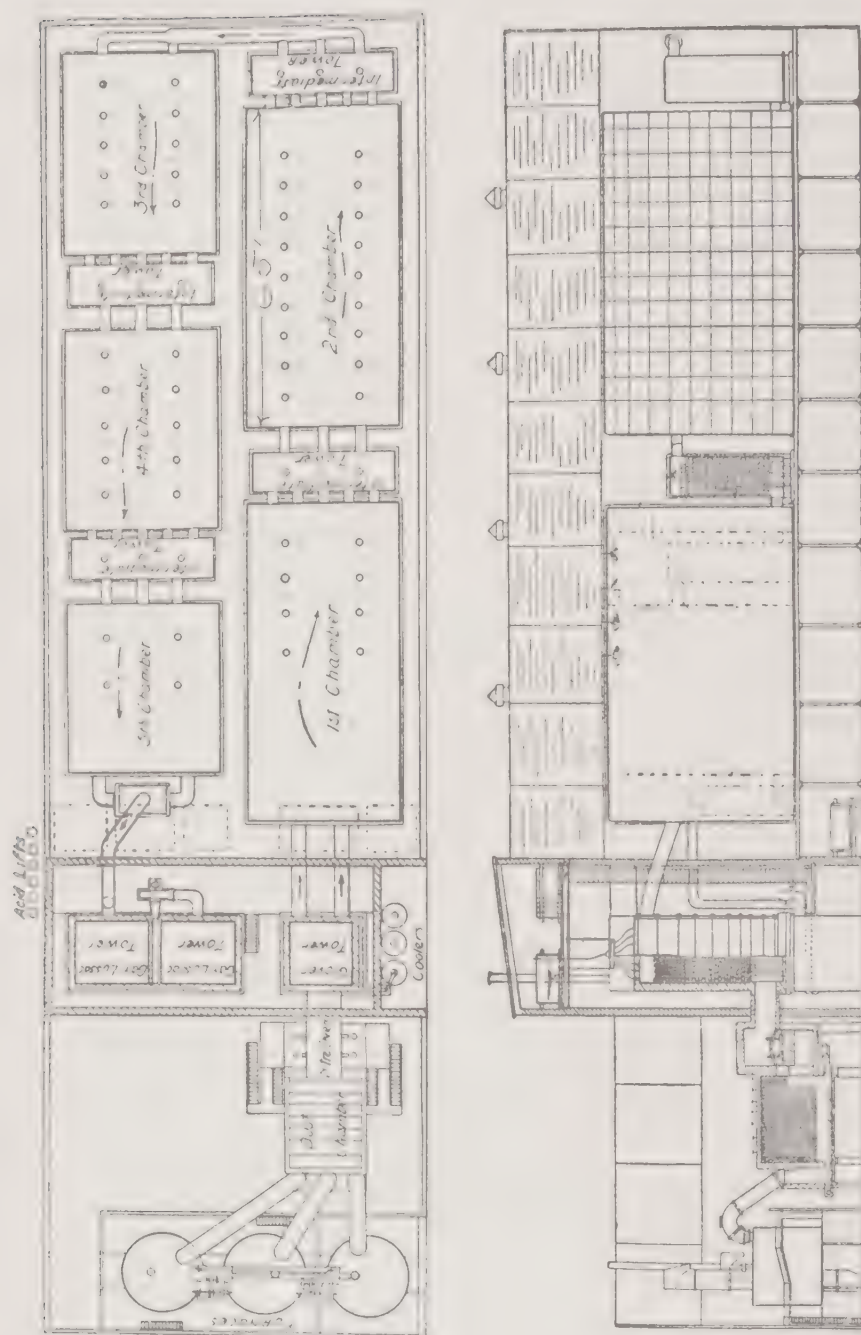


FIGURE 1.—A complete sulfuric acid chamber plant, with 3 furnaces, dust chamber, nitre oven, Glover tower, five rectangular chambers, the special intermediate towers (5), Gay-Lussac towers, acid lifts, acid coolers. One-third of the acid produced in this set (90 tons per day) is made in the intermediate towers; the first four are 25 feet high, 6 feet wide, 28 feet long. (Courtesy of the Chemical Construction Corp., New York.)

now almost obsolete; and the burning of the cheaper ammonia to produce the necessary oxides of nitrogen permits a more intensive reaction; a slightly greater loss of nitric oxide can be tolerated. One pound of ammonia [NH_3] produces as much nitric oxide as five pounds of 100 per cent sodium nitrate.

A plant does not necessarily confine itself to one process,¹ but may operate both types of plant, diluting the stronger contact acid with the weaker chamber acid to produce medium strengths.

The principal commercial strengths of chamber acid are:

50° Bé. acid (chamber acid)	62.18%	H_2SO_4^2
55° Bé. acid (chamber acid)	69.65	"
60° Bé. acid (chamber acid, concentrated by heat)...	77.67	"
66° Bé. acid (oil of vitriol, concentrated by heat)....	93.19	"

A table for converting Baumé degrees to specific gravities will be found in the Appendix.

The strength of the acid is judged by a hydrometer test, with the hydrometer graduations in Baumé degrees (*see* Chapter 46). For the strengths up to 66° Bé. (93.19 per cent H_2SO_4), that is satisfactory; between 93.19 and just above 100 per cent H_2SO_4 , the electrical conductivity is a reliable and convenient method. Between 8 and 56 per cent free SO_3 the oleums may be tested with a hydrometer; below and above these figures, by titration. The commercial strengths of oleums are 15, 20, 26, 30, 45, 60, and 65 per cent free SO_3 .

SET OF SULFURIC ACID CHAMBERS

In order to manufacture sulfuric acid by the chamber process, there are needed: (a) burners for lump ore, rotary burners for fines, or special burners

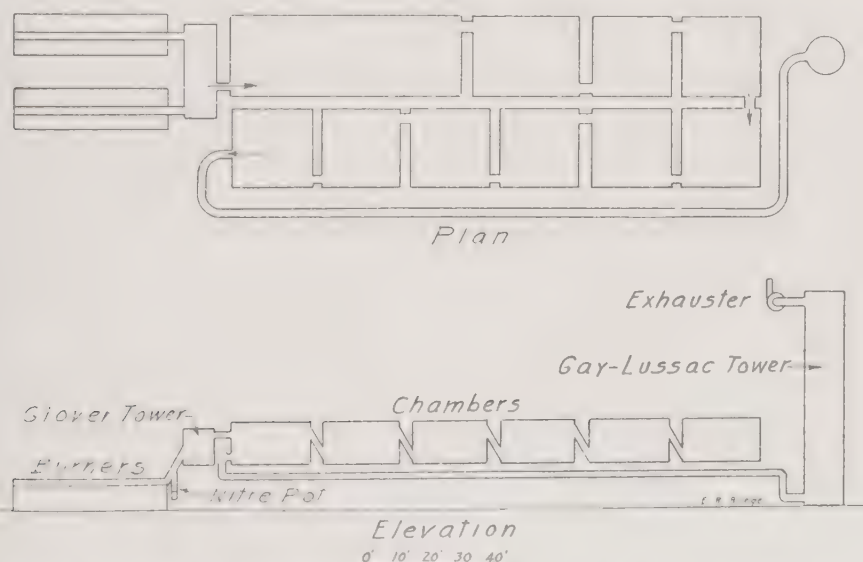


FIGURE 2.—Plant for the manufacture of sulfuric acid by the chamber process.

¹ A list of the sulfuric acid plants in the United States will be found in *Chem. Met. Eng.*, 37, 50 (1930).

² Taken from the table published by the Manufacturing Chemists' Association of the United States. The relation of Baumé degrees and decimal specific gravity is as follows: Baumé degrees = $145 - (145 \div \text{specific gravity})$.

for sulfur; (b) a Glover tower; (c) a set of chambers; (d) one or more Gay-Lussac towers; (e) several auxiliary devices. (See Fig. 1.)

A specific set with daily capacity of 17 tons of 55° Bé. acid per day is shown to scale in Figure 2, and will be described; it will reflect the older practice. With this plant as a basis, the important modern developments will be readily placed and appreciated.

(a) Lump Burners. The source of sulfur dioxide in this 17-ton set is iron pyrite, FeS_2 , a very heavy, yellow ore, also called fool's gold. In size it is two-thirds nut, one-third pea. There are 30 burners, mere fire-places, each 5 feet broad, 6 feet deep and 6 feet high, with cast-iron grate bars and brick walls. Each receives a single charge of 1000 pounds per day. In order to start the ore, coke must be used, but once started, the ore supports its own combustion. Air is admitted under the grate bars, through a number of 2-inch holes which may be closed at will; the amount of air, and therefore the percentage of sulfur dioxide in the "burner gas," is regulated here. The burner gas with all its heat passes through a flue to the nitre pot, and thence into the base of the Glover tower. The iron is left on the grate in the form of the dark red oxide, Fe_2O_3 , which is discharged by shaking the grate. The reaction is $4\text{FeS}_2 + 11\text{O}_2 = 2\text{Fe}_2\text{O}_3 + 8\text{SO}_2$.

(b) Glover Tower. The Glover tower is a rather low rectangular box made of sheet lead supported by an outer steel frame and filled with quartz of assorted sizes. The acid collected at the base of the Gay-Lussac tower, rich in nitrous fumes, passes down the tower together with water, which

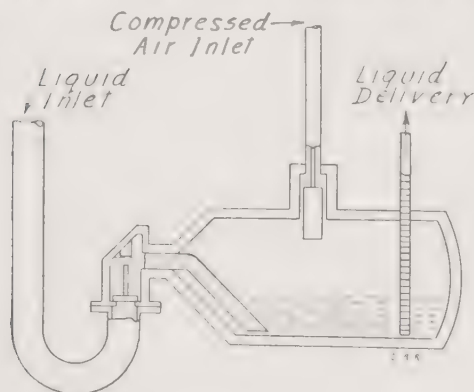


FIGURE 3.—Blowcase for the elevation of sulfuric acid.

dilutes it and releases the dissolved nitrogen oxides. Up the tower passes the hot burner gas, carrying away the nitrogen oxides, and the water as steam. The Glover acid, on issuing from the bottom of the tower, passes through lead coils laid in running water, in order to cool it from 130° F. (54° C.) to 60°–70° F. (15°–21° C.). The cold acid is elevated by means of an automatic blowcase or a pump to a small tank over the Gay-Lussac tower, from which it is fed gradually through a distributor and an elaborate system of small pipes, each with a U-bend forming a seal, to every part of the packing in the tower. (See Fig. 3.)

(c) Chambers. The set has a large first chamber, with a floor 75 feet by 26 feet; a second chamber, 35 feet by 26 feet; and eight smaller chambers 26 feet by 28 feet. The height for all is 14 feet. The walls, roof, and floor

are of sheet lead, with the seams "burned" with lead, that is, melted with an air-hydrogen blowpipe; the lead is supported on an outer frame of wood or steel.

(d) **Gay-Lussac Tower.** The Gay-Lussac tower is used to recover as far as possible the nitrogen trioxide gas which leaves the last chamber with the nitrogen and excess oxygen, and would otherwise be lost to the system. The tower is 70 feet high, circular, and has a diameter of 13 feet. It is made of lead supported by an outer steel frame and is filled with quartz lumps, graduated in size, the largest being on the bottom. The cold Glover acid passes down the tower; up the tower pass the gases from the tenth chamber; the descending acid dissolves the nitrogen oxides, and allows the other gases to escape. The absorption is never perfect. Nitrogen oxides, in the proportion of $\text{NO} + \text{NO}_2$, form a yellow gas which is soluble in cold 60°Bé . sulfuric acid; the strength of the solution after passage through the tower fluctuates between 1 and 2 per cent apparent N_2O_3 ; this is now the "Gay-Lussac acid"; when water is added to such a solution, the gas is liberated and passes out.

The marketable chamber acid is allowed to accumulate in the chambers, so that its level gradually rises. When the amount collected is sufficient, it is syphoned or pumped to a storage tank, or to a railroad tank car, ready for shipment. It is customary to use the chambers for storing the acid as it is made.

Since 1918, acid-proof masonry has been successfully applied to the construction of Glover and Gay-Lussac towers.³

(e) **Auxiliary Devices.** These are a nitre pot, set in an enlargement of the flue leading the burner gases to the Glover box; acid eggs, or blowcases, into which acid is run by gravity, and forced up a long pipe to the desired point by compressed air; and distributors, to divide the acid from a central pan at the top of a tower into a number of small streams so that all parts of the packing may be wetter. The nitre pot has been replaced by an ammonia burner, in many cases, and the blowcases are giving way rapidly to the small centrifugal pumps of special metal. In addition, a Venturi pipe to measure the flow of gas, a fan to pull the gases through the chambers and towers, and lead syphons and lines to transfer the finished acid to storage tanks are necessary.

In brief, then, the manufacture of the acid is as follows: Pyrite or sulfur is burned to produce sulfur dioxide; this oxide combines with oxygen and water, by the agency of nitric oxide, to form sulfuric acid. The Gay-Lussac tower is not needed for the reaction itself; it is a device for conserving the nitrogen oxides. Control of the reaction, so that the loss of the costly nitre gas will be a minimum, is the main problem.

In the cast-iron nitre pot, the nitre is covered with Glover acid; the heat of the burner gas causes the gradual evolution of nitric acid, which passes into the burner gas and there is reduced by sulfur dioxide to nitric oxide and dioxide. These nitric oxides, with more or less moisture, are commonly spoken of as "nitre gas." The ammonia burner may be placed where the nitre pot was, and its gas delivered to the sulfur gas entering the Glover

³ "Recent developments in the manufacture of sulfuric acid," S. F. Spangler, *Ind. Eng. Chem.*, 21, 417 (1929).

tower; a not infrequently selected place of entry however is after the Glover, just at the entrance to the first chamber.

The observations made by the "chamber man" in order to follow the reaction are: analysis of burner gas; temperature in the first and last chambers; sulfur dioxide analysis in the last chamber; color of the gas, and fog, at the exit of the last chamber, observed by means of a glass globe set in the line; depth of the yellow color of the gas at the exit from the Gay-Lussac tower; specific gravity of the drips from a lead table placed inside each chamber and from two tables in the first chamber; titration of Gay-Lussac tower acid for nitrogen trioxide; gauge reading at the Venturi meter, readings at the ammonia oxidation unit.

Travel of the Gas. The burner gas goes to the Glover tower, where it denitrates the mixture of Gay-Lussac acid and water; also it concentrates the acid, carrying the steam into the first chamber, so that in spite of the addition of water at the top of the Glover, the acid issuing from its base is as strong as the Gay-Lussac acid which was fed in. In addition to this steam, exhaust steam or atomized water⁴ is admitted into the first chamber right over the inlet pipe, and into the subsequent chamber in a corresponding position. The reaction proceeds vigorously in the first chamber; its intensity is gaged by a thermometer or pyrometer. The steam or sprayed water is regulated so that the specific gravity of the acid is about 55° Bé. To be sure that "newly made" acid is tested, sloping lead tables are built into the chamber with a connecting pipe to the outside, so that the "table drips" may be led, through a seal, to a hydrometer jar.

The gas then passes into the second chamber through a short, wide pipe; then into the third, and so forth. In each chamber a heavy mist forms, which slowly settles, leaving the unchanged gases saturated with moisture. The droplets which settle are sulfuric acid with an amount of dissolved water depending on the amount of steam present. Too little steam causes a strong acid to settle, which on reaching 60° Bé. will dissolve the nitrous acid and form chamber crystals (nitrosyl sulfuric acid, HNSO_5). Too much steam may act also to remove nitrous acid by solution in the water of the weak acid, and this will dissolve the lead. The drips indicate in which direction the danger lies. In the last chamber the gas still should be about 2 per cent SO_2 and the temperature 80° F. (27° C.), if the first chamber is 115° F. (46° C.).

Composition of the Burner Gas and Fluctuations. The burner gas should have a composition of 8 to 11 per cent SO_2 by volume for proper working of the chambers. Atmospheric air contains 20.8 per cent oxygen by volume; when using pyrite, 8 volumes are required for the formation of sulfur dioxide, and 3 volumes to form iron oxide; hence there is left 9.8 per cent oxygen on the original volume; when using sulfur, 11 volumes of the oxygen may be used, with none wasted to the cinders, to give 11 per cent SO_2 gas. For the further formation of sulfuric acid, 4 volumes (or 5.5) of oxygen must be provided, plus a slight excess. The nitre gas is furnished by the Gay-Lussac acid diluted by water as it enters the Glover tower, sup-

⁴It is better to spray in water than to feed steam, but special sprayers are required. Steam is easier to apply; its drawback is that it adds heat to a system which needs cooling.

plemented by enough dry nitre plus Glover acid, or oxidized ammonia, to replace that lost to the atmosphere at the exit from the Gay-Lussac tower. If this normal loss alone were to be made good, the quantity would be constant, say 12 pounds of nitre an hour. But there are irregularities which cause greater losses over short periods. The most interesting of these is the diurnal fluctuation, due to the change in the temperature of the outside air from day to night; and what is more, it does not follow night and day closely, but lags about 6 hours behind. To maintain the proper intensity of reaction, the nitre during the cool period (night) must be decreased, and during the warm period (day) it must be increased. Taking all the causes of loss of nitre gas together, a nitre consumption of 2 to 3 per cent on the sulfur burned for brimstone burning plants is considered normal, and one of 2.5 to 5 per cent for plants running on pyrite and by-product smelter gas.

Aside from general unavoidable irregularities, each set has its own peculiar defects due to its age. Leaks develop through the chamber walls, and to prevent a loss of gas, the fan speed is increased. As a result the gas is leaner, and other guiding temperatures must be settled as being the most advantageous. In other words, each set has its own "best" temperature.

The set described provides 10.1 cubic feet of chamber space for each pound of sulfur burned per day, if the ore delivers 38 per cent of its weight to the combustion air; this would be an average performance. Sets are compared as to intensity of working by means of this figure; the effort is to make it small.

A chamber plant is very quiet: almost nothing can be heard except the overflow water from the acid cooling tanks, and the periodic escape of compressed air from the automatic acid elevators.

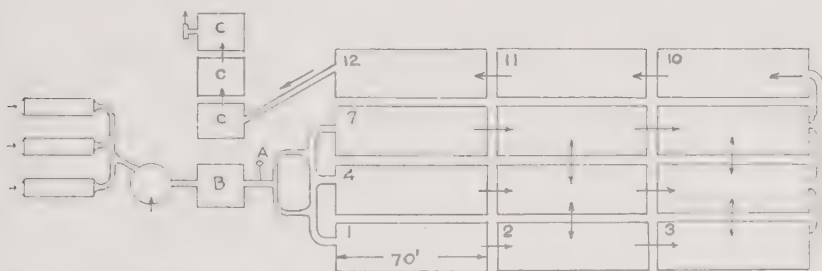


FIGURE 4.—Plan for the brimstone-burning chamber set. B, Glover tower. C, C, C, Gay-Lussac tower sections; A, ammonia burner.

Brimstone-burning plant. Another chamber set in which *brimstone* is the source of sulfur dioxide will be described. Its burners are slowly rotating, long, cylindrical steel drums, with the long axis horizontal; the brimstone is melted. A regulated stream of air passes over the sulfur, keeping the blue flame going, and sweeping the combustion gases gently into a combustion chamber, a tall cylindrical tower set upright, which also receives the combustion gases of two more similar burners. Any entrained sulfur mist is burned here, with the aid of secondary air. The gas testing 11% SO_2 enters the Glover tower; it then receives the nitric oxide from an ammonia burner, and passes into the chambers.

There are 12 chambers, each one 70 feet long, 24 feet wide, and 28 feet high; they are arranged in four groups of three chambers each. The gas enters numbers 1, 4, and 7 from the main header, and travels from each of these through two more chambers before reaching the return header; hence the gas has now swept through 9 chambers. The return header collects the partly reacted gas and sends it all through number 10, from there to number 11, then through number 12, thence to the Gay-Lussac, and finally through the fan to the exit. The operation is more intensive than in the previous set, the temperatures are higher, and the nitre gas loss between 3 and 4%.

The brimstone charge is 3000 pounds per hour; the ammonia burned is 500 pounds NH_3 per day; the yield is 4.85 pounds of 50° B . acid per pound of sulfur burned, an astounding figure, since the theoretical yield is 4.92 pounds. The space efficiency is 7.83 cubic feet per pound of sulfur burned per day. The temperatures for the first three chambers are 1st, 232° F. [111° C.]; 2nd, 232° F. [111° C.]; 3rd, 200° F. [93.3° C.]; in the last three, they are 10th, 180° F. [82° C.]; 11th, 165° F. [73.89° C.]; 12th, 112° F. [44.4° C.]. The Gay-Lussac tower works at 80° F. [26.67° C.]; this tower is built in 3 sections standing side by side, the gas traveling up one section, down the second, and up the third. The sections are 20 feet square, and 35 feet in height; the packing is a silica brick. Water is introduced at the top of the Glover, in order to dilute the Gay-Lussac acid and liberate its nitre gas; this is supplemented by water sprayed directly into the chambers, through an atomizer with a porcelain nozzle. Thirty-three per cent of the acid is made in the Glover tower, and 20 per cent in the first chamber; the acid as it leaves the Glover is clear and colorless. All the acid made in the chambers passes through the Glover; the made acid is drawn off from there through coolers, to storage. Such a set runs very smoothly, and the labor requirements are small: one man to bring the sulfur to the hopper feeding the burners, another man for supervision and testing.

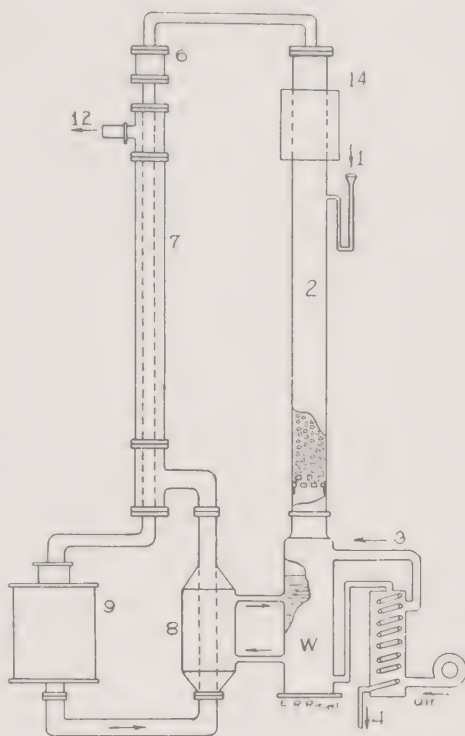
Ammonia Oxidation Unit. Numerous ammonia oxidation units have been installed to supply the nitre gas required for the chamber operation. In such a unit, a mixture of air and ammonia gas (11 per cent NH_3), preheated by the outgoing gases, passes through fine mesh platinum gauze raised to red heat. At this point, the reaction $4\text{NH}_3 + 5\text{O}_2 = 4\text{NO} + 6\text{H}_2\text{O}$ takes place, with an evolution of 214.2 Calories. This is enough heat so that with proper construction and preheating the gases no additional heat from an outside source need be applied.

The unit constructed by the Chemical Construction Corporation, is shown in Fig. 5.⁵ It is designed to receive aqua ammonia, rather than anhydrous ammonia; in the stripper column, warm air removes (strips) NH_3 from the solution; the mixed ammonia and air preheated in the interchanger (7), enter converter (9), where the reaction to form nitric oxide takes place. The outgoing gases reach first the heater (8), wherein the weak aqua ammonia is heated to boiling, then the heat exchanger (7), before passing out through (12) to the Glover tower. As the gases pass through, an oxidation of the nitric oxide to form a mixture of higher oxides takes place.

⁵ U. S. Patent 1,748,646.

A picture of the converter and further discussion of ammonia oxidation are given in Chapter 6, where the manufacture of nitric acid by ammonia oxidation is presented.

FIGURE 5.—A "Chemico" oxidation unit. 1, entry of ammonia aqua; 2, stripper; 3, warmed air; 4, exhausted liquor to waste; 6, filter; 7, heat exchanger; 8, heater for the ammonia liquor; 9, converter; 12, outlet of nitre gas to the chambers; 14, condenser to hold back excessive moisture. *W*, weak ammonia liquor.



Another oxidation unit works on anhydrous ammonia directly.⁶ The liquid anhydrous is vaporized in a coil heated by part of the outgoing gases, passes an oil filter and enters a mixer (a length of aluminum pipe) which also receives the preheated and filtered air required. The mixture, with a temperature of 250° C. [482° F.], enters the converter, whose contact material is an 80-mesh gauze of four layers, made of platinum-rhodium alloy (Baker number 750), with strands .003 inch in diameter. At bright cherry heat, about 900° C. [1652° F.], the conversion is 95 to 96%. A unit burning 24 pounds of NH_3 per hour has a gauze cylinder 4 inches in diameter, and 7 inches high; its life is 6 to 12 months. The warmed anhydrous ammonia gas must pass an expansion valve, which is regulated by a Smoot regulator. The volume of air fed in by a separate blower is filtered at its entry to the blower, and again after it is hot, through a (Mid-West) filter having an oiled filtering surface for the retention of dust particles. The ammonia-air mixture is constantly analyzed and its composition indicated by a Ranarex analyzer (Chapter 46). The operation of the oxidation unit is entirely automatic; the chamber man sights the platinum gauze for color, and reads the Ranarex; adjustments for different poundages to be burned are readily made.

⁶ "Ammonia oxidation makes further gains in chamber plants," Theodore R. Olive, *Chem. Met. Eng.*, 36, 614 (1929).

SOURCES OF SULFUR DIOXIDE

The main source of sulfur dioxide is the burning of brimstone or of iron pyrite. In 1929, 66 per cent of the sulfuric acid made was from burning brimstone, 17 per cent from pyrite, and 17 per cent from smelter gases; for 1935 the figures were very similar. In 1939, the acid made from sulfur gas manufactured in zinc and copper smelters was 778,441 tons 60° Bé strength. Before the war of 1914-18 only 2.2 per cent of the acid was made from brimstone, the rest from pyrite or other sulfides, partly imported. In 1939, it is estimated that 61.0% of the acid was made from brimstone, 26.2% from pyrite, and 13.1% from by-product gas from zinc and copper smelters, making no allowance for acid made from sulfur recovered in gas purification or in petroleum refining. In 1941, 69.3% of the total acid made was made from brimstone, 18.7% from pyrite, 11.4% by-product smelter gas, and 0.6% from recovered hydrogen sulfide. A burner for sulfur is described in Part II of this chapter. Acid for pharmaceutical use was always made from brimstone.⁷ The sources of brimstone sulfur are discussed in Chapter 38.

Pure pyrite, FeS_2 , contains 53.4 per cent sulfur. It is seldom found pure, but if it contains 42 per cent sulfur or more it is suitable for sulfuric acid manufacture. The arsenic content is important; less than 0.2 per cent arsenic is desirable for the chamber process, and imperative for the contact process.

Iron pyrite is produced domestically, and is also imported. The amount imported from Spain in 1935, a typical year, was 387,140 tons; these imports supply the plants along the Atlantic seaboard advantageously. Figures for domestic production and importations are shown in Table 1.

TABLE 1.—Sources of Iron Pyrite.*

	1939	1940
Produced in the United States.....	516,108	617,513 long tons
Imported	482,336	407,004 long tons

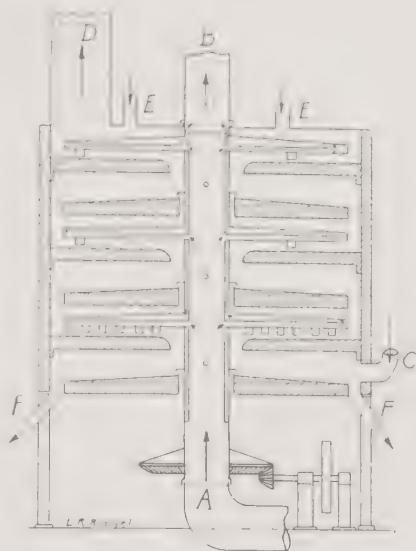
* Minerals Yearbook, 1941.

Nearly all the States have iron pyrite rock; the production is of importance in New York, Missouri, Colorado, Illinois, and others. Tennessee is the leading producer, if flotation concentrates are included.

The Rotary Burner for Fines. Pyrite fines, the screenings from the lump ore, were at one time waste; the lumps were saleable, while the fines, unavoidably formed in the process of mining and transporting, could not be used because they choked the fire in the lump burner. The fines were disliked also because of the considerable quantity of iron oxide dust which is carried by the combustion gas. They are now burned in automatic rotary shelf burners (see Fig. 6) with horizontal shelves and air-cooled raking arms (Herreshoff, Wedge). The spent cinders are discharged continuously from the lowest shelf. With the development of the rotary shelf burners, and of the Howard dust chamber, which permits the fine dust to settle out and thus cleans the gas inexpensively, the fines have become as valuable as the lumps.

⁷ U. S. Pharmacopœia, Philadelphia, J. B. Lippincott, 1926.

FIGURE 6.—A rotary shelf burner for fines; A, inlet for cooling air; B, outlet for cooling air, after it has swept through the rotating arms; C, inlet for combustion air; D, outlet for sulfur dioxide gas; E, inlet for the ore; F, outlet for the cinders.



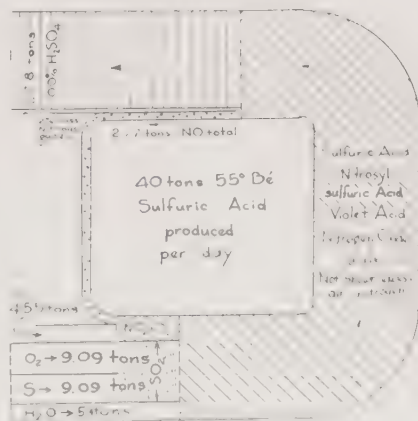
The Cottrell electrical precipitator⁸ is successfully used for removing iron oxide dust from burner gas.

A method and apparatus for recovering sulfur dioxide from waste ferrous sulfate liquors have been devised.⁹

The purification of refiner gas or natural gas by the phenolate process (see Chapter 14) leads to the recovery of vast amounts of hydrogen sulfide, which is now a source of sulfur dioxide for several acid plants.

Flash Combustion Roasting of Iron Pyrite.¹⁰ An entirely new way to burn pyrite, adapted primarily for the very fine powder obtained by the flotation process of treating the ore, has been developed. It consists in feeding the pyrite powder with a small supply of compressed air into a combustion chamber; secondary combustion air comes up from below. The ore

FIGURE 7.—Diagram of materials for a chamber plant which is to produce 40 tons of 55° Bé. sulfuric acid per day. The relations given are the theoretical ones, inasmuch as most plants almost reach these figures. Water of dilution amounting to 12.2 tons is not included in the diagram.



⁸ Chapter 43.

⁹ See flowsheet, *Chem. Met. Eng.*, 42, 699 (1935).

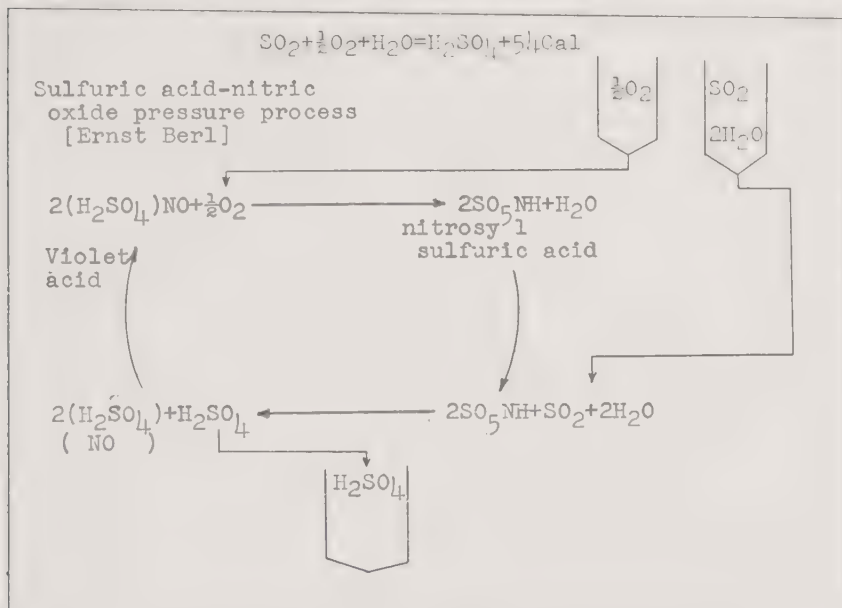
¹⁰ Article by Horace Freeman, *Am. Inst. Chem. Eng.*, 26, 148 (1931); also article by W. M. Cobleigh, *Ind. Eng. Chem.*, 24, 717 (1932), and "Flash roasting of pyrites concentrates in sulphite pulp manufacture," by Horace Freeman, *Chem. Met. Eng.*, 44, 811-813 (1937).

sents the reaction mechanism for the chambers when operated at the usual pressure,¹² that is, one or two inches of water below atmospheric pressure. The reactions explain themselves.

If this process is operated under pressure, the space yield rises; thus there are produced

at 1 atmosphere pressure,
at 25 atmospheres pressure.

18 lbs of 60° Bé. acid/hour, 100 cubic feet
62,300 lbs. of 60° Bé. acid/hour, 100 cubic feet



Under a pressure of several atmospheres, the oxidation of the violet acid will be performed by the oxygen itself, but not exclusively; to a certain extent, the oxidation will be by NO_2 , as in the atmospheric chamber process. The liberated NO will be oxidized at an accelerated pace, due to the higher pressure, so that even for that mechanism, the higher pressure will increase production per unit chamber or cell space

FIGURE 9.—Reaction cycle in the sulfuric acid-nitric oxide pressure process; the pressure may be 10, 25, or 50 atmospheres.

or 3000 times more. The cycle of reactions for the pressure system is given in Fig. 9. There is no large-scale installation which embodies the pressure process at the present time (1942); it offers however very large yields for a small-sized apparatus, and a new and promising application of the sulfuric acid-nitric oxide process. It will be noted that the nitric oxide does only a small part of the oxidation, most of it being done by the oxygen; hence the Gay-Lussac tower would be small.

MODERN DEVELOPMENTS IN THE CONSTRUCTION OF CHAMBER SETS

Mixing of the gases is essential; this has led to the construction of intermediate towers, of small cubic capacity, placed between the chambers. (See

¹² The theory of Raschig, in which nitrous acid is the working agent, is summarized in the *Journal of the Society of Chemical Industry* for 1911, p. 166

Fig. 1.) The towers are packed with stoneware rings, forcing intimate contact of the reacting gases, which results in a high production of acid.¹³

A great deal of acid is made in the Glover tower, perhaps 10 per cent of the total. The conditions in the cooler parts of the tower are propitious: the temperature is high enough, water is abundant, the contact of sulfur dioxide, air, and nitrous acid intimate. This suggested the scheme of providing a second Glover tower, in which more acid might be made. The Pratt converter is based upon this consideration. The first chamber is very large, comprising 75 per cent of the total chamber space. The reacting gases leave this chamber and enter a quartz-packed "converter" tower in which intimate mixing is afforded and a considerable amount of acid made. From the tower the greater part of the gases is returned to a fan which feeds them into the first chamber again; a smaller portion passes to the second and third chambers.

The Anaconda Copper Mining Company has gone not merely a step further, but all the way: its plant is all towers; there are no chambers. The acid is made in acid-proof brick cells. The cooling is no longer by air, but

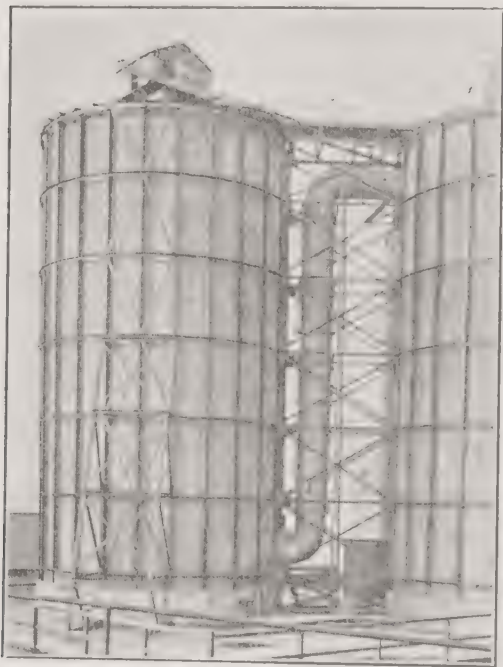


FIGURE 10.—Gaillard-Parrish sulfuric acid chambers, erected 1930, in London, England. Chambers are equipped with Gaillard turbo-dispersers for internal dispersion of pre-cooled sulfuric acid. (Courtesy of Mr. Andrew M. Fairlie, Chemical Engineer, Atlanta, Ga.)

by chamber acid which passes down the cell towers; this acid is then itself cooled in worms laid in running water, and used over and over again. The acid made is thus circulated ten times. Per pound of sulfur burned per 24 hours, there is only 1 cubic foot of reaction space.

For a number of sound reasons, F. J. Falding has constructed chambers 75 feet tall, a single chamber followed by a special cooling tower taking the place of a number of smaller ones, with excellent results.

In order to use the gas from copper blast furnaces for the manufacture

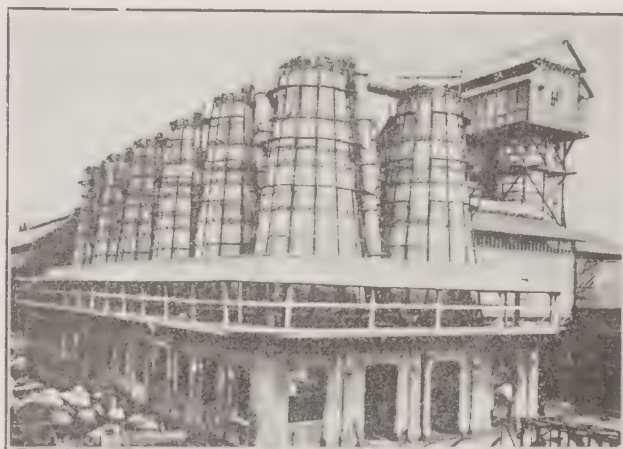
¹³ See "The Manufacture of sulphuric acid in the U. S.," A. E. Wells and D. E. Fogg, *Bur. Mines Bull.* No. 184, (1920), p. 108.

of sulfuric acid, in spite of its fluctuation between 4 and 8 per cent sulfur dioxide, A. M. Fairlie has devised a method of control which depends on the maintenance of desirable ratios between the sulfur dioxide in the gas entering the Glover tower and the gas in the first chamber. This is accomplished by putting varying amounts of nitre to meet the variations.¹⁴

The Gaillard-Parrish cylindrical sulfuric acid chamber¹⁵ has the turbo-disperser of Gaillard mounted at the top of the tower-like chamber devised by Parrish. (See Fig. 10.) The reaction takes place in the liquid phase; the disperser delivers inside the tower finely divided cooled acid, which forms a fog, filling the chamber. It is on the surface of the droplets of this fog that the reaction takes place. A considerable volume of acid is withdrawn from the base, cooled in lead coils laid in cold water, and pumped into the turbo-disperser; this acid absorbs much of the heat of reaction, and thus favors its progress. The chamber is also cooled at the top.

The Mills-Packard sulfuric acid chambers¹⁶ are shaped like a truncated cone with the large end down; the average dimensions would be about 32 feet diameter at the base, 27 feet diameter at the top, and 50 feet for the height, with a cubical content of about 19,000 cubic feet (Fig. 11). The outside

FIGURE 11. — Twelve Mills-Packard sulfuric acid chambers, truncated cone-shaped outside water-cooled, free from enclosing structures; the Gay-Lussac and Glover towers are to the right. (Courtesy of Mr. Andrew M. Fairlie, Chemical Engineer, Atlanta, Ga.)



walls are cooled by a curtain of water extending from the top all the way down. The removal of heat promotes the reaction, and in a small chamber space, more sulfur dioxide is oxidized than would be the case without water cooling.

Both the Mills-Packard and the Gaillard-Parrish chambers are erected in the open, as Figures 10 and 11 indicate, so that the expense of an enclosing building is avoided.

A "towerless" sulfuric acid plant has been described¹⁷ in which large condensing surfaces are produced by spraying made acid into the chambers;

¹⁴ Installed at the Tennessee Copper Co.; covered by U. S. Patents 1,205,733-4.

¹⁵ Percy Parrish, "Liquid phase operation of sulphuric acid chambers gains significance in Europe," *Chem. Met. Eng.*, 36, 68 (1929); also "Thermal aspect of liquid phase sulfuric acid production," 37, 93 (1930).

¹⁶ *Chem. Met. Eng.*, 37, 468 (1930); *Trans. Inst. Chem. Eng. (Brit.)*, 5, 42 (1927); *Chem. Met. Eng.*, 24, 786 (1921); and British Patents 247,744 and 239,397.

¹⁷ "The Watson towerless sulphuric acid plant, a new development of the chamber process," *Industrial Chemist and Chemical Manufacturer (London)*, p. 159, April, 1939.

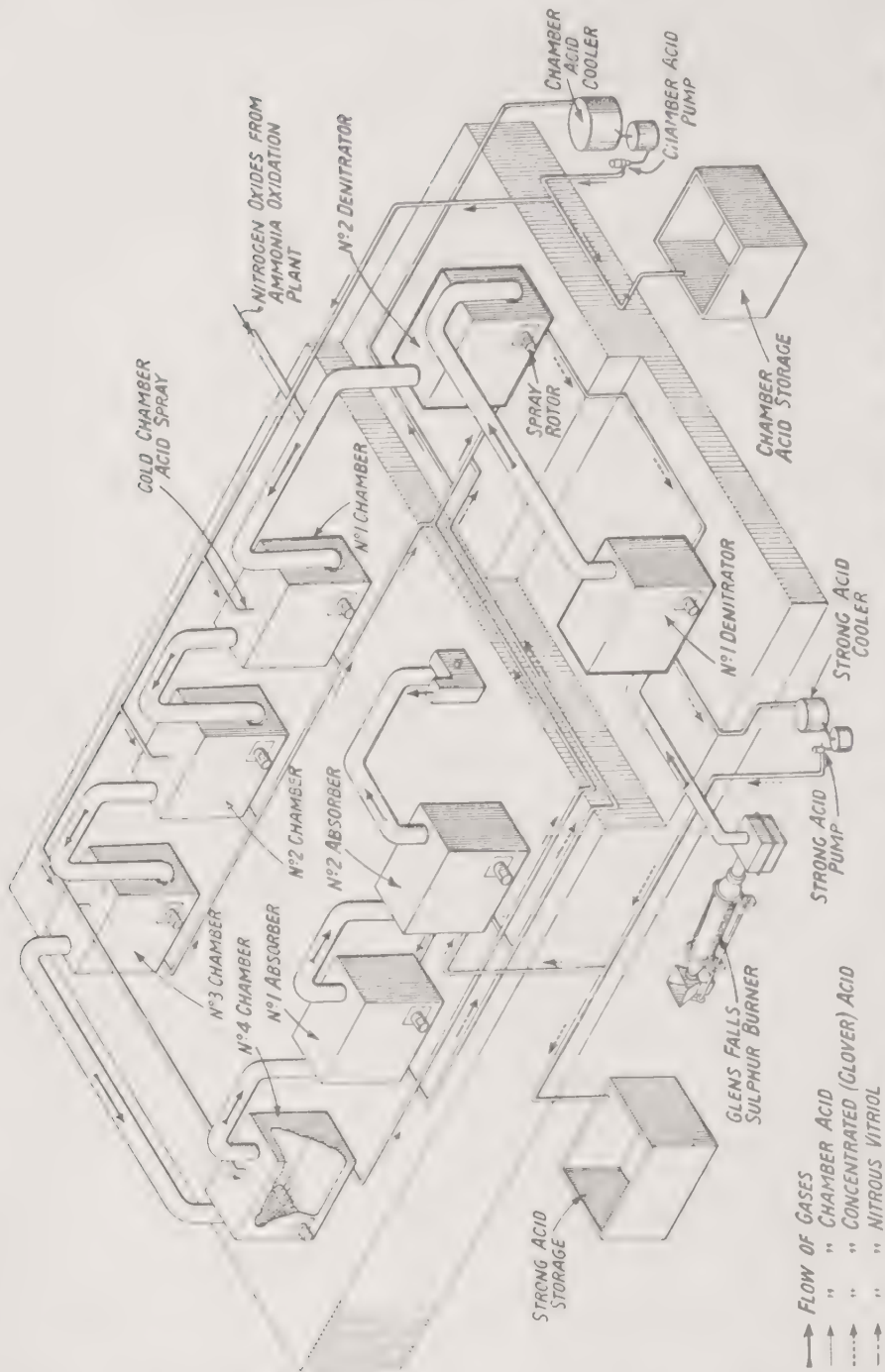


FIGURE 11a.—An isometric drawing showing the layout of the Watson towerless sulfuric acid plant and direction of flow of acid liquors and gases. (*The Industrial Chemist*, p. 159, April, 1939.)

the excessive heat generated is removed by first water-cooling the acid to be sprayed in. Such water as is needed is added as cold water, also in the form of a spray. In addition to this, the acid on the floor of the chamber is sprayed upward by means of silicon-iron rotors. The large surface area offered by the many droplets and the immediate utilization of the catalyst gases increase the speed of formation of sulfuric acid, so that a greater out-

put is obtained from the same space. Each chamber proper (4) is fitted with a spray rotor, cold-acid spray nozzles, and cold-water spray nozzles. No Gay-Lussac tower is used; instead, the gases finally travel through two absorbers, which are like the chambers except that they have no spray, but two bottom rotors; here the nitre is absorbed. The charged acid is mixed with chamber acid and flows to the denitrators (2) which take the place of the Glover acid, where it is sprayed by bottom rotors into the hot burner gases, giving up its nitre gas and much of its water. Counting only the four chambers which function solely as such, the space efficiency is 0.69 cubic foot per pound of sulfur burned per day. The emphasis, however, is less on space efficiency than on the absence of heavy and expensive towers. The towerless plant would be well suited for small installations; in April, 1939, it was estimated that a plant to produce 50 tons of sulfuric acid per week would cost in England 5,500 pounds sterling.

A comparison of the efficiency of the more important chamber systems is given below.

TABLE 1a.—*Efficiency of Sulfuric Acid Chambers System in Terms of Space.*

Chambers	Cubic feet of space per pound of brim- stone burned per 24 hours (annual averages)	Cooled by
Rectangular	7.5-10.0	air
Mills-Packard	2.5- 3.0	water
Gaillard-Parrish	2.5- 3.0	cold-acid circulation
Anaconda cells	1.0 (approx.)	cold-acid circulation

Two other processes deserve mention, although neither is in successful operation at the present time in the U. S.; they are the Schmiedel process,¹⁸ in which nitrosyl sulfuric acid is sprayed into the sulfur dioxide gas to provide as great a contact as possible; and the pressure process, designed for a 4-ton per day production,¹⁹ in which sulfur gas is introduced into a sealed tower 18 inches in diameter, which replaces the chambers. It is the rapid development of contact catalysis which has prevented the exploitation of these processes in the United States. The Schmiedel process is operated in some foreign plants.

Concentration. The chamber acid may be concentrated without expense for fuel from its normal strength of 53° to 60° Bé. by passing it through the Glover tower. It may be concentrated to the still more valuable 66° Bé. acid with the aid of coal or oil fire. In the cascade system, the acid passes through a series of pans set stepwise so that each pan overflows into the next lower one; the hottest fire is near the lowest one which contains the strongest acid. The pans are glass, silica or Duriron.

In the Chemico Concentrator²⁰ hot fire gases from an oil burner are passed through the acid, and remove water.

In another system, the gas from an oil burner passes up a tower 5 feet square and 39 feet high, packed with quartz, while the acid passes down the tower; water is carried out by the gases; they deposit such sulfuric acid

¹⁸ U. S. Patents 1,399,526 and 1,512,863.

¹⁹ U. S. Patent 1,513,903.

²⁰ The Chemical Construction Corporation, N. Y.

mist as they may form with water in a wetted coke box. The capacity for such a tower is high, 24 tons of 66° Bé. acid per day.

It is not possible to concentrate chamber acid above 97% by heat, because above such strength the acid decomposes.

Prices. The prices for raw materials vary on account of market conditions and for other reasons. The price of the product varies also, depending upon market conditions, length of contract, and on specifications. The figures below are intended merely to indicate the usual price range.

In 1940, domestic iron pyrite brought \$3.06 a long ton; its sulfur content was 41.7 per cent. The sulfur it contained cost, therefore, 0.32 cent per pound. Brimstone, which was quoted at \$16 a long ton in the same year, therefore costs 0.71 cent a pound. Chamber acid in 1939 averaged \$6.72 a ton; in 1935 the figure was \$7.83.

Ammonia was sold in large lots and on contract at 3.73 cents a pound, for the 100 per cent grade.

The cost of erection of a standard chamber plant was estimated at \$2,100 to \$3,000 per ton of 60° Bé. acid produced per day, prior to 1940.

PROBLEMS

1. In the brimstone-burning chamber plant described in the text, the number and dimensions of the chambers are given, as well as the pounds of sulfur burned per hour. Compute the total chamber space available; extend the weight of sulfur burned to 24 hours, and find the space efficiency figure, then compare it with the figure in the text.

2. Find the pounds of 50° Bé. acid which may be made from 1 pound of sulfur. What is the percentage yield, if for each pound of sulfur, 4.60 pounds of acid are made?

3. Find the weight of water which must be furnished per day for the amount of acid made per day in the brimstone-burning set.

4. In the same set, if the nitric gas loss is 3 per cent of total nitric oxide in the set, including the Gay-Lussac acid, what is the total nitric oxide present?

5. Burning a pound of NH_4 to nitric oxide is equivalent to potting how many pounds of sodium nitrate, 100 per cent pure? Check the figure given in the text.

6. In the burner house, six burners of the rotating type receive 1000 pounds of brimstone each, every hour. The gas passes to 14 Mills-Packard chambers. How closely will the resulting space efficiency figure agree with the figure given in the table in the text, for such chambers?

7. Set up factors for changing sulfur, by weight, to H_2SO_4 100 per cent by weight to 66° Bé. sulfuric acid, to 60° Bé., to 55° Bé., to 50° Bé. sulfuric acid. The percentages of H_2SO_4 for the several strengths will be found in the texts.

8. Let the volume of gas from the burners be 8 per cent SO_2 . In the first set described, in which the sulfur delivered to the gas is $30 \times 1000 \times 0.38$ per day, what is the weight of the sulfur equivalent, and of the sulfur dioxide produced, in pounds? What is the volume of the resulting 8 per cent SO_2 gas? The gram mole and the gram molecular volume in liters may be used, with a conversion figure taken from the appendix. For this purpose, assume that the gas is at STP. Let the 8 per cent gas be delivered through a 36-inch diameter line to the system; what is its velocity, in feet per second? To find it, compute the volume of 8 per cent gas served per second. If the gas has a temperature of 200° F. [93.3° C.] when passing through the 36-inch line, what is its velocity?

9. What is the cost of materials for making 40 tons of 50° Bé. sulfuric acid per day, by burning brimstone, when the latter is bought at \$16.00 a ton of 2240 pounds, plus 1 per cent for freight? The water is free.

10. The roof and the sides of the chambers are made of seven-pound lead, that is, of sheet lead weighing seven pounds to the square foot; the bottom is 10-pound lead. For the set of 12 chambers of the brimstone-burning plant, what is the weight of the lead required, and what is its cost, if the sheets as delivered are 6.5 cents a pound? An additional amount will be needed for the Gay-Lussac tower, for the Glover, and for the cooling tanks and their cooling coils at the foot of the Glover.

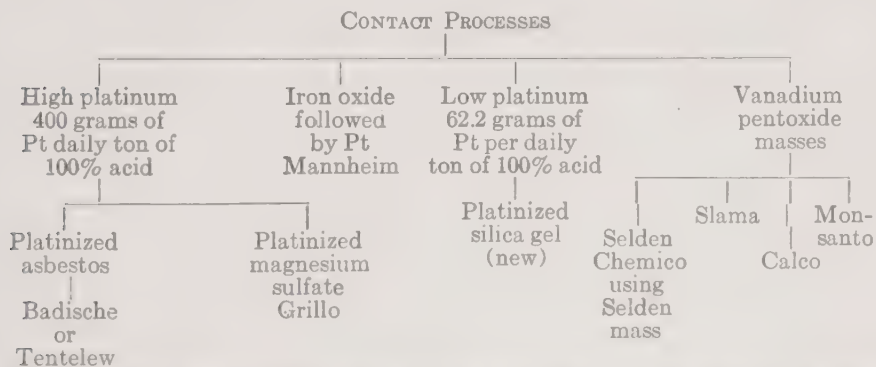
The difficult step in the manufacture of sulfuric acid by any process is the change of sulfur dioxide to sulfur trioxide. If sulfur burned to form at once the trioxide, there would have been no opportunity for many fine minds to exercise their inventiveness and ingenuity; but it burns to the dioxide only. In the chamber process, this is accomplished with the aid of nitrous acid; in the contact process, this same step is accomplished with the aid of a solid substance called the contact substance, because when sulfur dioxide and oxygen are in contact with it, at the proper temperature, they unite to form the desired sulfur trioxide, which, with water, gives sulfuric acid.

Chapter 1—Continued

Sulfuric Acid—Part II: The Contact Process

The contact process became a firmly established industrial process at the turn of the century; until about fifteen years ago, the contact material was mainly finely divided platinum on an asbestos carrier or on a calcined magnesium sulfate carrier. Iron oxide of secondary importance was as contact material. The situation has changed entirely since 1926, when the introduction of vanadium pentoxide as the contact substance took place.* This less expensive agent is not used as such, but is always supported by an inert carrier such as diatomaceous earth, which does not melt at the high temperatures [around 450° C. (842° F.)] employed. Its service has been so satisfactory that it may be estimated that in recent years, over half of the contact acid was manufactured with the aid of a vanadium pentoxide catalyst. For the last ten years, a very efficient platinum mass in the form of platinized silica gel has been available, but the vanadium masses have retained their preëminent position.

The various processes may be grouped as follows:



All the contact processes form sulfur trioxide, the anhydride of sulfuric acid. It is a gas at any temperature above 45° C. (113° F.) and atmospheric pressure. In water, it dissolves explosively, but in sulfuric acid of 98 per cent strength, it dissolves smoothly, and this acid is the common absorbent.

The reaction $2\text{SO}_2 + \text{O}_2 \rightarrow 2\text{SO}_3$, which takes place in the converter

* Vanadium catalysts were in use in Europe during the war of 1914-18 in special installations; they came into general industrial use in Europe in 1921.

(under proper working conditions), runs to 97 per cent completion at a temperature of about 450°C . (842°F .). The catalyst may be platinum,¹ vanadium pentoxide, or iron oxide. At temperatures appreciably below 450°C . (842°F .), sulfur dioxide escapes oxidation. At somewhat higher temperatures, the opposite reaction, $2\text{SO}_3 \rightarrow 2\text{SO}_2 + \text{O}_2$, takes place; the result in either case is the same, namely, the conversion falls below 97 per cent. The conversion figure is obtained by dividing the sulfur dioxide which is oxidized by the sulfur dioxide fed into the converter, and multiplying by 100. On closer examination, it is found that the rate of reaction $2\text{SO}_2 + \text{O}_2 \rightarrow 2\text{SO}_3$ is only moderate at 400°C . (752°F .), but increases enormously with a rise in temperature. Thus at 500°C . (932°F .) it is 40 times as great as at 400°C . (752°F .). By rate of reaction is meant the amount of sulfur dioxide converted in unit time. The opposite reaction, $2\text{SO}_3 \rightarrow 2\text{SO}_2 + \text{O}_2$, is also accelerated by a rise in temperature, but becomes appreciable only at much higher temperatures. For example, at 400°C . (752°F .) it hardly takes place at all; but at 550°C . (1022°F .), its rate is high enough to produce a fair amount of the lower oxide. Hence it would be advantageous to provide a temperature of 550°C . (1022°F .) to the gas as it enters the catalyst mass, and then after 80 per cent conversion or so, to cool the gas gradually, so that as it sweeps through the last portions of the mass, the temperature would be 425°C . (797°F .). In this way a rapid reaction, and at the same time a high conversion, should be attained.

The oxidation reaction is exothermic: $2\text{SO}_2 + \text{O}_2 = 2\text{SO}_3 + 45.2$ Calories. This heat must be dissipated in the proper degree to prevent excessive temperatures which would cause the reverse reaction $2\text{SO}_3 = 2\text{SO}_2 + \text{O}_2$ to proceed vigorously. More than enough heat is generated to maintain the apparatus at the proper temperature, and to preheat the incoming gases.

The catalytic reaction $2\text{SO}_2 + \text{O}_2 \rightleftharpoons 2\text{SO}_3$ is reversible. It is desirable to drive it to the right. The law of concentration effect (the mass law) requires that the concentration of one of the factors (SO_2 or O_2) be increased, if it is desired to increase the formation of the product. By increasing the concentration of the oxygen, more of the product is formed, while at the same time, the sulfur dioxide is nearly exhausted.² The burner gas contains 8 per cent

¹ The honor of having discovered that platinum catalyzed the reaction to form the trioxide belongs to Peregrine Phillips, Jr., of Bristol, England (1931). Platinumed asbestos was proposed first by the Englishman Jullion (1846).

² At any one definite temperature within the range concerned, and in the presence of the catalyst an equilibrium between the gases SO_2 , O_2 and SO_3 will be attained, provided enough time is allowed. The value for the equilibrium constant in the formula

$$K_p = \frac{(P_{\text{SO}_3})}{(P_{\text{SO}_2})(P_{\text{O}_2})^{\frac{1}{2}}}$$

using partial pressures in atmospheres, for the temperatures observed in practice, is:

Temperature	K_p	K_c
400°C .	467	109,700
425	255	61,000
450	145	35,300

Expressing the constant in terms of mols per cc., for the same reaction, the values listed under K_c are obtained.

The reader will please note that the expression applies to the reaction $\text{SO}_2 + \frac{1}{2}\text{O}_2 = \text{SO}_3$, not for the reverse reaction, nor for the reaction written with twice the number of molecules; for the latter the value of the constant will be the square of the above values; for the former, the reciprocal.

It may be well to point out that it is the constant K which does not change, while the absolute amounts of the three gases may be altered. If the concentration of oxygen is increased, the value of (P_{SO_2}) must decrease, to maintain the value of K , assuming the change in (P_{SO_2}) to be relatively small. This is what happens when a 100 or 200 per cent excess oxygen is provided. K may also be expressed

SO_2 which would require only 4 per cent O_2 for the reaction as written; but 10 per cent or more is always provided, an excess of over 150 per cent, thus insuring a high conversion figure.

The conversion depends furthermore upon the temperature, the period of contact, that is, the relation between volume of mass and cubic feet of gas, and upon the activity of the mass. The pressure on the gases is essentially atmospheric pressure.^{2a} The commercial installations illustrate all these factors.

The function of the contact substance is to adsorb the reacting gases at its surface; in the closer proximity which results, coupled with the high activation caused by the high temperature, the successful collisions are enormously increased in number, and the speed of reaction is correspondingly raised. In the case of platinum, surface adsorption is the only function. For vanadium pentoxide (or other oxides), it is more likely that the various oxides of vanadium do take part in the action; the higher oxides give up oxygen, but are continually reformed by the incoming oxygen, so that they are found unchanged after the reaction. It may be said, therefore, that the contact substance in any process is unchanged after a period of years. Commonly, the life of a mass is considered to be 10 years. The subject of poisoning is presented after the plants have been described.

Additional discussion of catalytic reactions will be found in Chapter 25.

THE CHEMICO PROCESS WITH VANADIUM MASS

A Chemico contact sulfuric acid plant of capacity of 17 tons 100 per cent H_2SO_4 a day will be described as typical of the most advanced practice of the present period. The plant is built entirely of iron and steel with some acid-proof masonry and ceramic packing in the drying and absorption towers. It has many features which will be welcomed by the student, particularly two: simplicity and compactness. The simplicity of the plant results largely from the use of brimstone sulfur as raw material; all auxiliary apparatus for cleaning burner gas from the combustion of pyrite is absent. Sulfur is melted, burned with air in the special spray burner; the combustion gases, with 7 or 8 per cent SO_2 , are cooled by passing them through a waste heat boiler, and then enter the converter. One important purification is provided,

in terms of the constants of the reaction rate, k_1 for the forward reaction, k_2 for the reverse reaction, then $K = \frac{k_1}{k_2}$.

The earliest researches on the value of the equilibrium constant, specific rate constant, and optimum temperature were those of Knietzsch, which formed the basis for the original contact process with platinum, the "Badische" process. A summary will be found in *Berichte der deutschen chemischen Gesellschaft*, v. 34, p. 4093 (1901). Knietzsch used flowing gases; more recently W. K. Lewis also used flowing gases, and reconsidered Knietzsch's data as well as set up new values by experiments. "Influence of reaction rate on operating conditions in contact sulfuric acid manufacture," *Ind. Eng. Chem.*, 19, 830 (1927) and 17, 593 (1925), where references to the work of Bodenstein on quiescent gases will be found. See also "reading references."

^{2a} The reaction $2\text{SO}_2 + \text{O}_2 = 2\text{SO}_3$ involves a decrease in volume, from 3 to 2, and one would expect that by running the process at a higher pressure, the rate of reaction would be accelerated, and the amount of material would be greater for a given space and contact mass. (Compare). Yet, as far as is known, all contact processes are run at near-atmospheric pressure, although proposals for, and trials at higher pressures have been made. The explanation probably lies in the slowness of one of the steps, of which the simple reaction given above is but a summation. The rate of diffusion of the incoming sulfur dioxide and oxygen mix to the surface of the catalyst is the slowest step, and it is this step which sets the pace for the reaction as a whole. The sulfur trioxide is strongly adsorbed on the surface of the catalyst, and it is through this layer of adsorbed sulfur trioxide that the incoming gases must diffuse. Increase in pressure would perhaps raise slightly the speed with which sulfur dioxide and oxygen travel through the sulfur trioxide layer, but the thickness of the latter would probably be increased, thus nullifying the first beneficial effect. [See *Trans. Am. Inst. Chem. Eng.*, 31, 223 (1935).]

however, namely, the air is dried. The drying avoids a number of difficulties, such as corrosion of parts and mist formation. The compactness of the plant is such that it is housed complete in what might be a good-sized room.

The diagrammatic flow-sheet in Figure 12, drawn from an actual plant, gives the sequence of operations. Melted sulfur is forced through the spray burner tip by a steam-driven turbine, submerged in the sulfur. The pressure on the melted sulfur is sufficient to drive it through a spiral cut in the adjustable valve rod (needle-valve type), so that it acquires a rotary motion and is discharged into the burner in a wide arc. Air is drawn upward through a packed steel tower, down which a heavy stream of cold 93 per cent sulfuric acid flows. The acid is circulated by a pump and is cooled by traveling through cast-iron cooling pipes laid in water. The dried air passes through a centrifugal blower and is delivered under forced draft to the sulfur furnace. The chamber for burning 5 (or 6) tons of sulfur per day is a cylinder lying on its side, 7 feet high and 17 feet long. It is of steel, brick-lined, with a terminal baffle. The gases leave the burner at 771°C . (1490°F .), and pass through a boiler, the tubes of which are surrounded with water. The steam generated is sufficient to melt the sulfur, run the steam turbine which runs the sulfur pump, and drive the main blower. By-pass flues around the furnace and waste heat boiler permit the regulation of the SO_2 concentration and the temperature of the gas entering the converter.

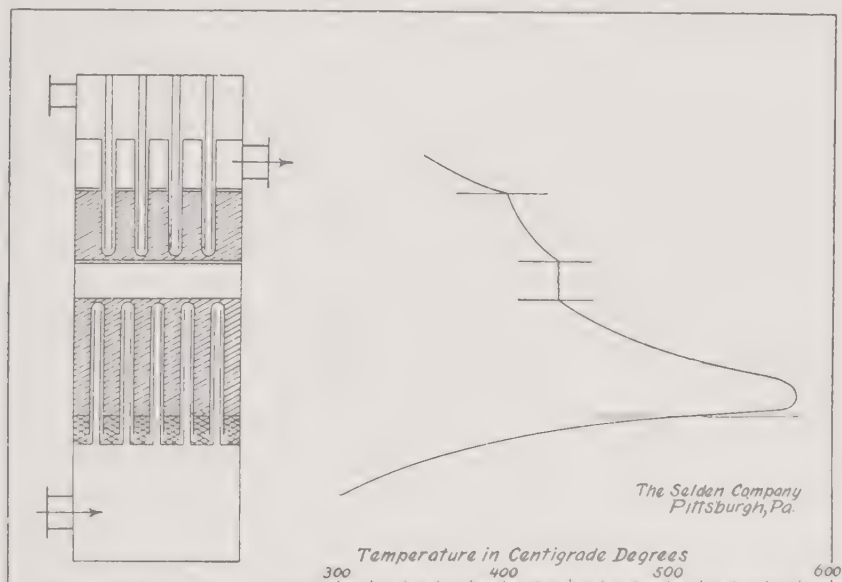


FIGURE 13.—The temperature for gas and mass at various levels in the "Selden" vanadium pentoxide packed converter for sulfur trioxide formation.

On leaving the boiler, the gases, with temperature 304°C . (580°F .), enter the converter, which carries the contact mass in two layers: 1800 pounds in the lower layer, 1200 pounds in the upper. One pound of the catalyst occupies one liter volume. The internal arrangements are as shown in Figure 13, which also gives the temperature for the gas (and mass) at various levels. The lower layer is cooled by the entering gases which reach

the top of the risers, and are deflected downward by means of the slender chimblees inverted over them. In the upper layer, the mass is cooled by a current of cold air. In the latest form of Chemico converter, shown later in the chapter, the upper layer is not cooled.

On entering the bottom mass, the gases are 493°C. (920°F.); 6 inches above the lowest layer, the maximum temperature is met, 593°C. (1100°F.). On leaving the bottom mass (upper portion) the gas is 482°C. (900°F.); the temperature in the top layer, where the conversion is completed, is 438°C. (820°F.).

The hot sulfur trioxide gas produced is cooled in a tubular heat exchanger by a stream of cold air from a fan, and is absorbed in a 98 per cent sulfuric acid tower. The latter is built of masonry, and filled with a checker-work of acid-proof bricks preceded by baffles, and surmounted by a bed of pebbles; a second level of baffles and pebbles insures mixing of the gas and good contact with the descending acid, so that the gas passing to the atmosphere through a stack is exhausted. The absorbing acid is diluted continuously by means of a weaker acid, such as chamber acid, or by means of water, in amount sufficient to keep the strength about 98 per cent. A heavy stream of absorbing acid is maintained, and its heat is continuously removed by passing through cooling pipes laid in water. The made acid is collected in a storage tank and transferred from there as needed.

When oleum is to be made, the oleum tower precedes the 98 per cent acid tower, and receives the gas first. The strength of the oleum is controlled by regulating the amount of acid fed to it: the stronger the oleum required, the slower the stream of acid. The gas leaving the oleum tower is still high in SO_3 content, and passes to the 98 per cent acid tower, where complete absorption takes place. The oleum leaving the oleum tower is collected separately, adjusted for strength if necessary, and pumped to storage or shipping tanks.

The acids are recirculated by means of self-priming, special metal centrifugal LaBour pumps. (See Chapter 41.)

The charge of sulfur for a 6 ton plant is 500 pounds every hour, dumped into the sulfur melting tank.

Control of Operation. The plant is practically automatic. No labor is required except for charging the sulfur. The operation of the sulfur burner is controlled by the temperature of its exit gas, which affects a resistance pyrometer; should the temperature drop, a Wheatstone bridge is unbalanced, and the current which can flow actuates a control which in turn allows more steam in the turbine, so that more sulfur is delivered to the burner. The volume of air is set. If the temperature of the exit gas rises, the opposite action results in decreasing the steam on the turbine.

The 98 per cent acid is controlled by measuring its electrical conductivity, and this is checked periodically by the "heat rise" test, as follows: 200 cc. of 105 per cent H_2SO_4 at temperature T_1 , and 200 cc. of the acid to be tested having temperature T_2 , are poured together and the temperature of the mixture, T_3 , noted. The value of R is found from the expression

$$R = T_3 - \frac{(T_1 + T_2)}{2}$$

Table 2 gives the percentage of the acid tested.

TABLE 2.—Testing of 98 Per Cent Acid for Strength by the Heat Rise Test.

<i>R</i>	Per Cent H_2SO_4	<i>R</i>	Per Cent H_2SO_4
2° C.	99.9	18° C.	97.5
4 99.5		20 97.3	
6 99.3		22 96.9	
8 99.0		24 96.4	
10 98.7		26 96.2	
12 98.4		28 96.1	
14 98.1		30 95.8	
16 97.8			

The strength of the 20 per cent oleum and of the 93 per cent acid is tested by a hydrometer.

The pressure of the air when let into the burner is 55 inches of water; on the gas entering the converter, 43 inches; leaving the converter, 28 inches; hence there is a differential of 28 inches due to the converter mass. Should this differential increase, it would mean that the mass was dirty, or had become plugged in some other way. It is then time to clean the mass, or to replace it.

Chemico Converter, full size. A Chemico converter for a plant having a capacity of 40 tons of 100 per cent H_2SO_4 per day, embodying the latest design, is shown in Figure 14. It will be noted that it has but one set of tubes, in the lower mass; the entering gases cool the mass, then pass through it, undergoing a preliminary conversion of about 85 per cent. The tubes and thimbles are longer than in previous designs; also the thimbles are "calorized"³ to increase their heat resistance. The packing of the mass is as follows: Over the perforated plate, a wire netting is placed, which carries $\frac{1}{2}$ -inch quartz pebbles to a height of 2 inches; over these, the catalyst is placed, uniform in size. The conversion is completed in the upper layer, which receives no cooling. Other details and dimensions may be obtained from the sketch.

Chemico plants in still larger sizes are available, with correspondingly larger equipment. For example the sulfur furnace for a plant burning 40 tons per day is 11 feet in diameter and 36 feet long.

The Chemico mass is being used increasingly in converters which do not have the inside risers and thimbles, but merely perforated shelves on which the mass is placed to form a layer 14 to 18 inches thick. There are two converters; in the first, the smaller one, the gas travels downward; in the second one, it travels upward.

Other Processes. An installation using brimstone sulfur with the Monsanto vanadium catalyst has a compactness⁴ similar to that of the Chemico process and an operation similarly neat. The Monsanto system has the two-pass converter system, that is, two converters with an inter-cooler between them is preferred. The first converter carries substantially 30 per cent of the catalyst and gives from 75 to 80 per cent of the conversion; the gas leaving this converter has a temperature of about 580° C. (1076° F). It is cooled to 400° C. (752° F.) in the inter-cooler and enters the second

³ A process patented by the General Electric Co. Aluminum is driven into the surface of mild steel, by heating, forming an aluminum alloy.

⁴ Daniel S. Dinsmore, *Trans. Am. Inst. Chem. Eng.*, 26, 158 (1931).

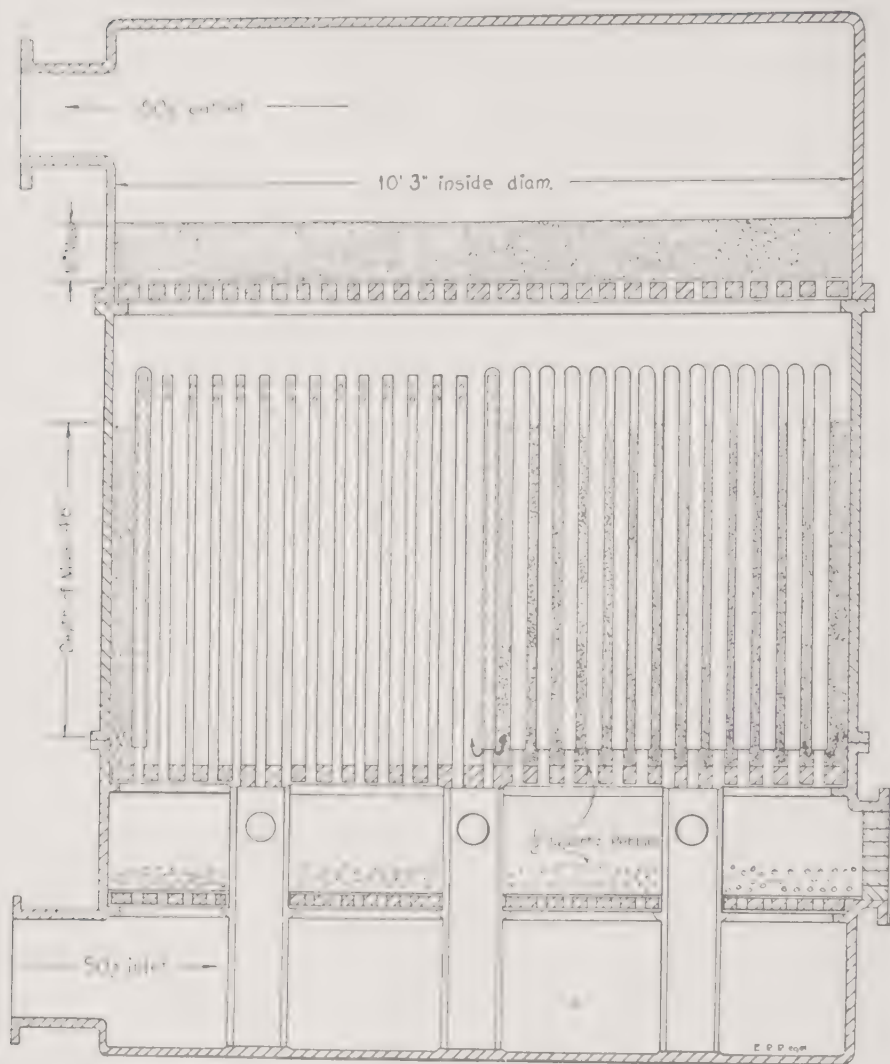


FIGURE 14.—The present form (1912) of the Chemico converter with vanadium pentoxide mass. It is circular in cross-section, has 716 thimbles and tubes, and a capacity of 40 tons per day. The thimbles and contact mass for the left half of the drawing have been omitted, in order to show the inner risers through which the gas enters. (Sketched through courtesy of the Chemical Construction Corporation, New York.)

converter at that temperature. In this one, the heat rise is moderate, 45 to 60° C. (81 to 108° F.), so that complete conversion of the small amount of SO_2 entering it is assured. Conversions of 97 and 97.5 are reported.

There is at least one plant using platinized silica gel which has internal cooling of a special type.

The Badische process, which uses platinized asbestos, installed in many American plants in the period preceding the war of 1914-18, operated with converters and transferers separate, with a by-pass to regulate the temperature of the gas.* Most of them continue in service.

* Described in some detail in the first edition of this book, where the purification of sulfur gas from Herreshoff and similar burners using pyrite is considered. Flow sheets for the Badische, Gailen-Schroeder and Mannheim systems will be found on page 150, Bureau of Mines Bulletin 184.

The Grillo-Schroeder system, installed in numerous American plants, which uses a calcined magnesium sulfate as platinum carrier, also continues for the most part to give excellent service.

The tendency is to change over to platinum when the opportunity offers itself.

Other systems that should be mentioned are the Tentelweil system (platinum) and the Mannheim system (iron oxide).

The Various Catalyst Masses. The catalyst masses of modern type best known in the United States are listed in Table 3, with their density, efficiency,

TABLE 3.— SO_2 to SO_3 Catalyst Masses.

	Apparent density of mass	Daily pounds of sulfur as 8 per cent SO_2 gas converted per liter of catalyst mass	Appearance
Selden mass, V_2O_5	0.46	5	Light greenish-yellow tablets $\frac{1}{4}$ " diameter
Monsanto mass, V_2O_5	0.56	5	Light green half-cyl- inders $\frac{3}{8}$ " length
Platinized silica gel	0.50	5+	Brown sand-like gran- ules $\frac{3}{8}$ " in length

For these three masses, a volume of catalyst fluctuating between 125 and 175 liters will be required for the production of one ton of 100 per cent H_2SO_4 per day.

and appearance. The efficiency is in terms of the daily pounds of sulfur as 8 per cent SO_2 converted per liter of catalyst mass.

Preparation of the Selden Mass. The vanadium pentoxide mass known as the Selden mass, developed by Dr. Jaeger, and used for the Chemico installation just discussed, is made as follows:⁵

"A." A solution of potassium silicate is sprinkled on diatomaceous earth; and the wetted particles are mixed by shoveling and raking.

"B." Potassium aluminate is made from potassium hydroxide and alumina, in the form of a solution.

Two equivalents of "B" are sprinkled on 5 equivalents of "A," and well mixed. The potassium aluminate and potassium silicate form a zeolite, of jelly-like consistency.

"C." Ammonium vanadate solution (3 equivalents) is added to potassium aluminate (1 equivalent) and potassium hydroxide, forming a thick gelatinous suspension which can just be poured; it contains a complex vanadium compound.

"C" is poured onto the soft zeolite-coated diatomaceous earth, mixed only slightly, without penetration. The lumps which form are compacted, screened, a small amount of stearic acid added (as lubricant) and formed into pellets $\frac{1}{4}$ inch in diameter. The pellets are calcined or sulfated by heating in a current of 1 per cent SO_2 , gradually raising the heat to 500°C . (932°F .) and increasing the proportion of sulfur dioxide. After calcination, the pellets are cooled in a current of air, and are packed in air-tight containers, for shipment. This is the finished catalyst, ready for the converter.

During the calcination, vanadium pentoxide is formed, but it remains in intimate contact with the other constituents of the pellets.

Badische Mass. A vanadium mass successfully used by the Badische Anilin und Soda Fabrik, in Germany, is made as follows: 316 parts of kieselguhr are mixed with a solution of 50 parts ammonium vanadate and

⁵ See German Patent 227,095 which has a sketch showing the radiating pyramids peculiar to this catalyst.

⁶ Taken from the court findings, Federal District Court for the Western District of Pennsylvania, in the case of the General Chemical Co. vs. the Selden Co.; the former claimed infringement of its patent 1,271,064 (Selden and Wolff). The court decided that the Selden Co. was not infringing. June 17, 1922. Since then, the case has been reopened and evidence taken before a special Master; in 1938, the controversy was finally settled in favor of the Selden Company.

56 parts potassium hydroxide; enough water is evaporated to allow the formation of granules. These are heated at 480°C . (896°F .) in 8 per cent SO_2 gas, then cooled in a current of air.

Platinum was the original contact substance for the oxidation of sulfur dioxide. It was dispersed on asbestos fibers or on magnesium sulfate crystals and then carefully calcined. Both these masses were and are efficient, but they contain so much platinum, in terms of sulfur treated that new installations would not be able to compete with the vanadium masses.⁶ A smaller amount of platinum dispersed on silica gel, with a final density of 0.7, was superior to platinized asbestos or platinized magnesium sulfate, and a silica gel mass, of more recent introduction, is a further improvement in the same direction.

A comparison of high platinum and low platinum masses is given on page 33.

The bugbear of the early contact operators was the "poisoning" of the platinum mass. There are two kinds of poisoning: temporary poisoning due to chlorine, which relieves itself as halogen-free gas sweeps through the converters; and permanent poisoning, due to arsenic. In the early days of the contact process, operators were surprised that burner gas from pyrite ore, fed to the new system, gave rise to difficulties, while in the chambers they functioned smoothly; the equipment for purification from chlorine and arsenic was soon evolved, and poisoning became a matter of faulty operation. Arsenic as arsine, AsH_3 , was avoided by not using iron for the coolers, so that condensed acid could no longer react with iron and form the hydrogen necessary for the formation of the gas. Lead is used instead.

PURIFICATION OF GAS FROM PYRITE ORE

Although at the present time (1941) 69 per cent of the total sulfuric acid is made from sulfur, there are still important installations in which iron pyrite, and especially pyrite fines, is the source of the sulfur gas. The purification of such gas must be performed with greater care and carried further, in order to use the gas in any contact system. How long the lavish use of elemental sulfur can continue is a serious consideration, for the resources of mineral sulfur are distinctly limited.⁷

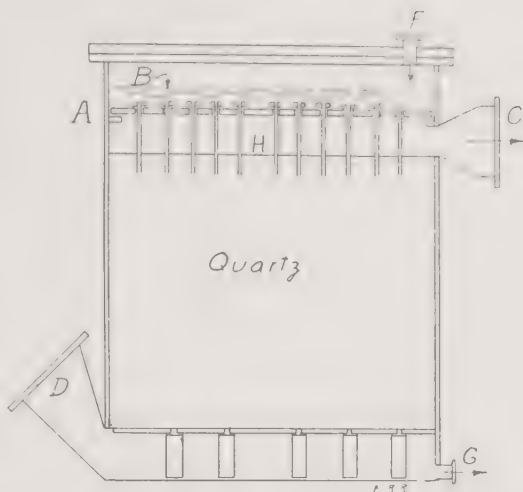
The gas from a Herreshoff rotary shell burner for fines (page 24) or from flash combustion is rid of its iron oxide cloud in dust chambers, or dust collectors, with or without a "hot Cottrell" precipitator following, all working on the hot gas. The gas next passes through short lead towers, meeting a flow of sulfuric acid, which cools the gas somewhat and removes the arsenic in the form of oxide; this tower, it may be noted, imitates the Glover tower. After this, the gas is cooled in water-cooled 8-inch lead pipes, to room temperature; it then enters coke-packed lead boxes, a wet box followed by a dry one, to remove chlorine, present in the form of hydrogen chloride, and to arrest the acid mist; the clean gas then enters the blower which feeds it to a drying tower with 62° to 66°Bé . (81.3 to 93.2 per cent) sulfuric acid as the drying medium. (See Fig. 15.) The gas is now ready for the converters; it

⁶ This is disputed, on the basis of a number of factors. See "Platinum vs. vanadium pentoxide as catalysts for sulfuric acid manufacture," A. Paul Thompson, *Trans. Am. Inst. Chem. Eng.*, **27**, 264-309 (1931).

⁷ "Economic position of sulfur," A. M. Taylor, *Ind. Eng. Chem.*, **24**, 1116 (1932).

FIGURE 15.—The drying tower;

A, circular plate bearing the porcelain tubes; B, level of the acid in the acid chamber; C, outlet for gas; D, inlet for the gas; F, inlet for the acid; G, outlet for the acid; H, upper level of the quartz packing.



may be preheated within the converter, as indicated in the Chemico construction, or by outside multi-tubular heat exchangers.

Alternate arrangements provide for water-washing in a tower just beyond the "hot or dust Cottrell," and this tower is followed by a second Cottrell, called the "moisture Cottrell."

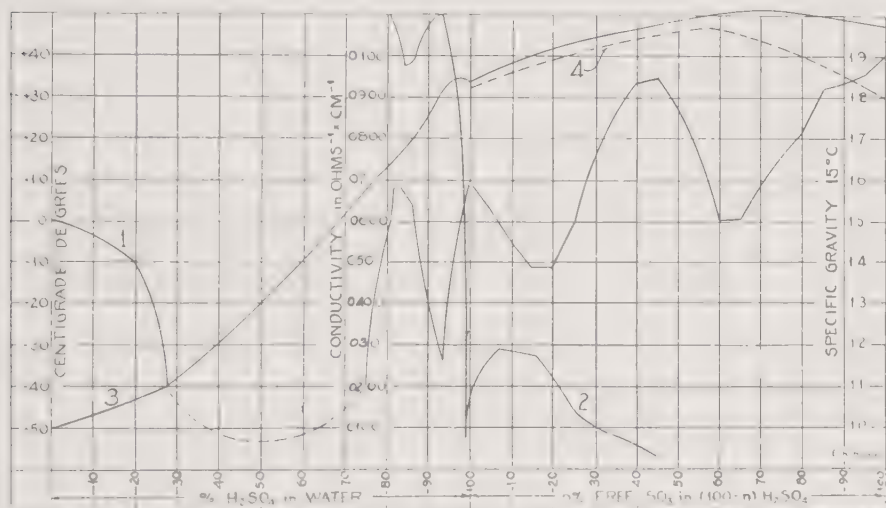


FIGURE 16.—Physical properties of sulfuric acids and oleums of various concentrations. 1, melting points (Knietzsch); 2, conductivities in reciprocal ohms (Landolt-Börnstein Tabellen); 3, specific gravities at 15° C.; 4, at 45° C. (Knietzsch).

The melting points for sulfuric acid of various strengths and for the oleums are extremely irregular; they are shown in Figure 16 by means of a graph. The specific gravity of the acids increases gradually to 1.8415 for the 97.70 per cent H_2SO_4 , which is the maximum; it then decreases slightly to the 100 per cent acid. As a result, the specific gravity as a measure of

strength over that range (96 to 100 per cent) might lead to gross errors; for that reason, conductivities are used instead.

The oleums also have a maximum specific gravity, more pronounced at 45° C. (113° F.) than at 15° C. (59° F.), as indicated in the figure.

YIELDS

A conversion of 97 per cent of sulfur dioxide to the trioxide is good practice. The unconverted gas is lost to the atmosphere on issuing from the last absorber. When sulfur as brimstone is the starting material, additional losses are only those due to the impurities in the brimstone, which remain in the melting tank, and generally are below 1 per cent on the weight of brimstone. The over-all yield may be about 95 or 96 per cent.

When iron pyrite is used as fines, there is a loss of about 2 per cent sulfur to the cinders. Losses occur in the scrubbing towers, coke boxes, electrical precipitators, and to a slight extent in the drying tower, so that an over-all yield of 90 to 92 per cent would be fair.

The cost of raw materials has been mentioned previously. The selling price for oleums is higher than for 66° Bé. acid, which in turn is higher than for the weaker acids; the price is roughly proportional to the sulfur trioxide content, except for the strong oleums, which are considerably higher. For example: 50° Bé. acid, \$6.75 a ton; 60° Bé., \$13.00; 66° Bé., \$16.50; 20 per cent free SO₃ oleum, \$18.50; 40 per cent oleum, \$42.00, all for tank car lots. These are the average prices for 1941. Acids of 66° Bé. and higher strengths are stored and shipped in steel tanks, weaker acids generally in lead-lined tanks. Smaller lots are shipped in glass carboys. Acid from 61° to 65° Bé. may be shipped in steel tanks if the acid contains an inhibitor (against corrosion).⁸

Concentration of Diluted Sulfuric Acid. In many operations, the sulfuric acid functions as a water-remover, while in others, it may remove water and have another function besides. The water taken up by the acid dilutes it, and it is essential that it be removed, so that the acid, restored to its former, higher strength may be used over again. In nitrations, in which mixed acid is generally used, there results a spent acid containing very little nitric acid, and with its sulfuric acid diluted. The concentration of spent acid becomes a major process in times such as the present, when large quantities are required, because transportation by freight, and the time required for such transportation, must be reduced.

In the Kalbpery concentrating tower the rising, hot combustion gases from an oil or other burner come in contact with the descending acid; water is driven out while strong acid collects at the base of the tower. The gases leaving the tower pass through a coke box or a Cottrell precipitator in order to deposit the mist. In America, the tower has been successfully used for the production of 96.5 to 97 per cent sulfuric acid from spent acid containing 68 to 70 per cent,* while in England, Parrish, a well known engineer, prefers

* Regulation of the Bureau of Explosives, Interstate Commerce Commission. Inhibitors are organic substances, such as sulfonated slaughter house waste, used in small quantities. "Practical application of inhibitors in pickling operations," F. N. Speller and E. L. Chappell, *Chem. Met. Eng.*, 34, 421 (1927). See also "reading references." The statement is made that 59 or even 58° Bé. acid is regularly shipped in steel tank cars without any inhibitor.

* Page 138, "The manufacture of sulphuric acid in the United States," by A. E. Wells and D. E. Fogg, Bureau of Mines, Bulletin 184 (1920) where a plan and elevation of the complete concentrator is shown.

to concentrate only to 90 to 92 per cent by any device which brings hot gases and the acid in contact,[†] and prefers a pot still, or a special vertical-tube concentrator with especially wide tubes for higher strengths. The Chemico Drum type concentrator (Fig. 16b) has been used with success in the United States as well as in other countries. The entire unit is constructed in the shape of a single cylindrical tank, with the exception of the electrical precipitator which removes the mist from the final gas. The acid compartments are lined with lead and acid-proof masonry, and the furnace end with fire and insulating brick. The combustion gases from the burner travel through iron and acid-proof iron pipes. The acid is concentrated in two stages; the highest strength is the acid in the compartment nearest the

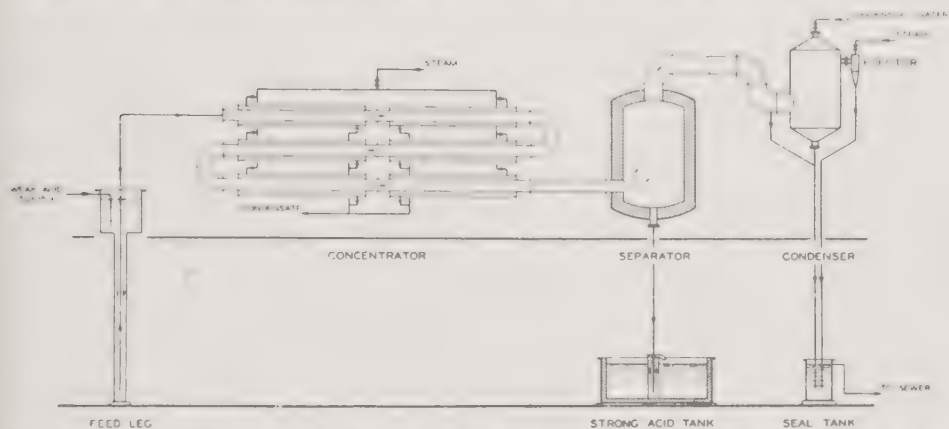


FIGURE 16a. Diagram of the "Chemico" sulfuric acid concentrating process, flash film vacuum type. (Courtesy of the Chemical Construction Corporation, New York.)

furnace which receives the hottest gas. All the gas and vapors leaving the first compartment enter the second compartment, where they contribute to the evaporation, yet lose instead of gain in sulfur trioxide content. The gases escaping through the stack of the electrical precipitator are fire gases and water vapor; acid which collects at its base is fed to the second acid compartment. The electrical precipitator may be omitted. Due to the blast of air and fire gases, the concentrating temperature is about 100° F. (37.78° C.) below the corresponding boiling point recorded in the tables for the particular strengths. The result is high heat efficiency. Some of the hot gases from the burner may be by-passed to the second or low-stage drum compartment, so that the evaporative work done therein may be regulated. The depth of the seal at the various gas inlet pipes is very slight, so that the back pressure is slight and power is a minimum.

The Chemico Flash-Film Vacuum-type Concentrator works under a vacuum induced by a steam jet condenser and barometric leg. The acid, lifted from the feed leg by the vacuum, cascades from one pipe to the next, over half-moon dams just indicated by a vertical line in Figure 16a. The concentrating pipes are acid-proof iron, steam-jacketed, with concentric steel pipes and packing glands. The amount of feed acid entering in

[†] "Concentration of sulphuric acid," modern plant development, by P. Parrish, *The Industrial Chemist* (London), 17, 41 (1941).

measured quantity is balanced against the heat input and vacuum to regulate the strength of the finished acid and the output from the unit. The flash-film concentrator is the proper choice where steam is cheap and water is plentiful.

Other processes are the cascade system, using quartz, Duriron, or other acid-proof metals; the Gaillard and the Kessler, both used mainly in Europe; the du Pont falling film concentrator, the Simonson-Mantius concentrator, and others.

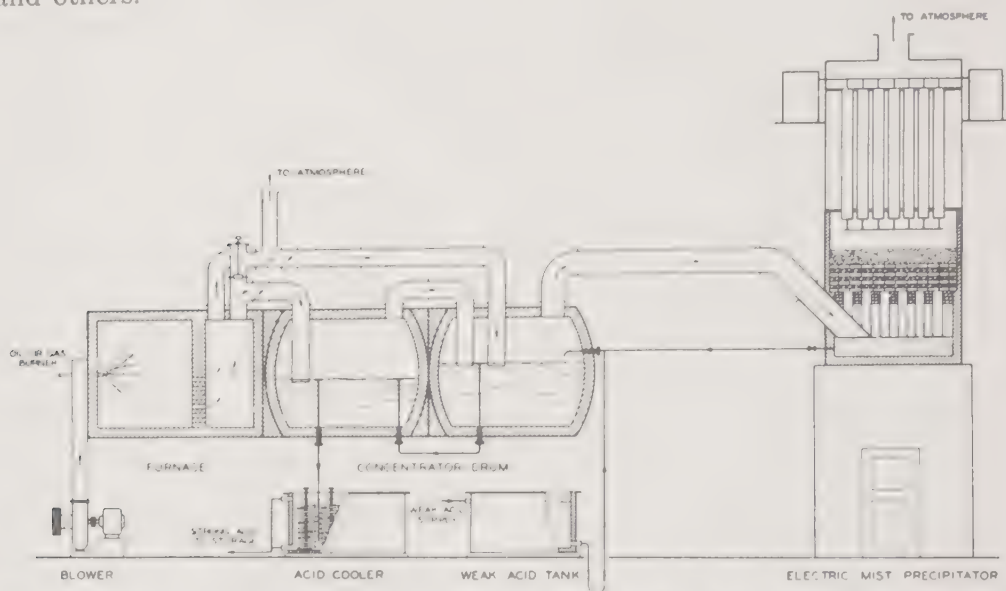


FIGURE 16b.—Drawing of a diagrammatic cross section of the latest design "Chemico" drum type sulfuric acid concentrator. Note the cooling coils for the strong acid leaving the first compartment (see text). (By courtesy of the Chemical Construction Corporation, New York.)

Recovery of Acid from Waste Products. There are processes which leave a sulfuric acid not only diluted but charged with impurities, such as tarry matter from the treatment of petroleum fractions. Some of these sludge acids are so difficult to separate into acid and sludge that it has been found advantageous to make sulfur dioxide out of residual acid (with or without auxiliary sources of sulfur dioxide), and remanufacture sulfuric acid from it in a vanadium type converter. There is produced clean and strong sulfuric acid, and a second product, a granular fuel. This is the Chemico sludge conversion process† devised by the late Dr. Hechenbleikner.

The sulfuric acid in copperas may now be recovered by roasting the copperas with pyrite in rotary furnaces, or by heating the previously dehydrated copperas with coal, under definite conditions.

THE RÔLE OF SULFURIC ACID

The uses of sulfuric acid are as varied as chemical technology; it is among the acids what lime is among the alkaline agents. If it is required merely to provide an acid state, sulfuric acid is chosen, provided it is not

† "Production of contact sulfuric acid from refinery acid sludge," by S. F. Spangler, Proc. 14th annual meeting Amer. Petroleum Institute, October 26, 1933, with a diagrammatic lay-out; or "Sulfuric acid from refinery sludge," an illustrated flow sheet, *Chem. Met. Eng.*, 48, 144 (1941).

unsuitable for special reasons. Many of its numerous applications are given in subsequent chapters. The production of sulfuric acid has been stimulated by war demands; in 1941, there were produced 10,944,000 tons 50° Bé. acid, an increase of 19 per cent over 1940, which in turn was 11.8 per cent higher than 1939.⁹ The estimated distribution is shown in Table 4.

TABLE 4. *Estimated Distribution of Sulfuric Acid Consumed in the United States, in Short Tons of 50° Bé. Acid.⁹*

Consuming industry	1940	1941
Fertilizer	2,260,000	2,500,000
Petroleum refining	1,260,000	1,400,000
Chemicals and defense	1,120,000	1,450,000
Coal products	900,000	940,000
Iron and steel	1,200,000	1,450,000
Other metallurgical uses	640,000	800,000
Paints and pigments	580,000	700,000
Industrial explosives	170,000	190,000
Rayon and cellulose film	470,000	555,000
Textiles	125,000	165,000
Miscellaneous	460,000	550,000
	<u>9,185,000</u>	<u>11,040,000</u>

The weak acid from the chambers has remained important because a dilute acid is required in the manufacture of superphosphate of calcium, a fertilizer. The standard chamber plant has the advantage of having no license fees to pay; the newer processes of necessity involve such payments which the acid produced must carry.

For many purposes, such as nitrations and sulfonations of organic substances, a strong acid is required, such as 98 per cent H_2SO_4 or an oleum; the contact process must furnish these. Furthermore, an oleum may be used to bring a weak spent acid to the reaction strength,* so that here also, the product from the contact plants offers an advantage; it may be said in fact that contact acid will do everything that chamber acid does; but the converse is not true. Finally, contact acid is very pure, and is selected for certain uses for that reason.

Sulfuric acid is no longer indispensable for making nitric acid of 50 and 61 per cent strengths now that the catalytic oxidation of ammonia has been perfected. For the manufacture of 95, 98 and similar nitric acids, sulfuric acid remains **necessary**.

Sulfuric acid occupies its important position because the raw materials are cheap, the methods of manufacture are highly developed, and no fuel is required, except for a small amount of power. When close to smelters, the raw material for producing the sulfur dioxide, may be said to cost nothing at all. The degree of perfection reached in both chamber and contact processes is remarkably high. The plants are practically automatic. Hand labor is needed to charge the sulfur to the melting tank; for the burners for fines, an operator must bring the ore to the top of the burners, by means of an electric truck. From that point on, the process runs by itself. As to supervision, one chamber man can watch and regulate three sets; in the contact process, one operator takes care of one or several

⁹ *Chem. Met. Eng.*, 49, February, 1942.

* The H_2SO_4 of limited applicability, for a balance must be maintained; a volume of acid greater than can be used must be avoided.

units, by reading pressure gages, thermometers and thermocouples, by making chemical or thermal analyses on the sulfur dioxide gas and exit gas, and by hydrometer and conductivity readings. Some of these means of control are automatic or automatically recording, simplifying the supervision still further. A small force of laborers is required for clean-out gangs, and skilled labor for repair gangs. Labor-saving devices and automatic continuous operation distinguish the sulfuric acid industry even in an age which is characterized by them.

OTHER PATENTS

U. S. Patents: 1,660,511, on the automatic heat exchange converter for contact process; 1,675,308, on the micro-porosity of vanadium mass structure, with 23 examples of preparation formulas; 1,675,309, vanadium pentoxide masses on quartz as carrier, with several examples; 1,691,123, also on vanadium pentoxide masses with porous structures; 1,657,754, on vanadates and tungstate for the catalyst mass, with 20 examples; 1,657,753 and -4, 1,695,285, 1,696,546, 1,701,075, all on vanadium masses; 1,741,310, on stabilizers in vanadium masses; 1,518,913, on vanadium mass to be preceded by some platinum; 1,450,661, on construction of converter, as also 1,685,672, 1,660,511, 1,857,308; 1,862,746, on drying tower construction and operation (*see also* 1,384,566, 1,824,896); 1,912,832, manufacture of sulfuric acid by means of nitrogen compounds, to Andrew M. Fairlie; 1,995,292, manufacture of sulfuric acid; 2,028,739, sulfur dioxide from Spanish pyrite, removing fluorine by silica, and otherwise purifying the gas; 2,008,761 and 1,970,923, process and apparatus for producing sulfur trioxide; 2,042,675, making sulfuric acid from a sulfur dioxide containing organic impurities; 1,995,360, 2,023,203, 2,028,416, making sulfuric acid or sulfur dioxide; 2,001,359, making concentrated sulfuric acid or oleum from sulfur dioxide regenerated from sludge in petroleum refineries, to the late Ingenieur Hechenbleikner; 1,996,764, production and purification of sulfur dioxide from similar spent acid; 2,044,960, production of sulfur dioxide and iron oxide; 2,030,885, apparatus for burning sulfur; 1,942,817, catalytic apparatus; 1,971,465, catalyst for use in the contact method of making sulfuric acid, containing thallium and vanadium; 2,030,021, method and apparatus for the production of sulfur dioxide, by roasting ore; 2,198,795, on tray type sulfuric acid converter; 2,172,617, for making high strength H_2SO_4 ; 2,258,938, on a nitric oxide-sulfuric acid process; 2,255,445, sulfuric acid and iron oxide from waste pickling acid.

German Patents: 459,978, sulfuric acid made in towers by an excess of nitrous gases; 463,828, on chamber acid; 455,075, for atomizing sulfuric acid; 467,587, on making all the acid in the Glover tower; 466,578, making oleum by contact process; 516,764, on a catalytic mass containing chromium hydroxide; 517,965, on a rotating oven for concentrating sulfuric acid.

PROBLEMS

1. Let it be required that a plant producing 10 tons of 100 per cent H_2SO_4 daily be erected. The brimstone is to be shipped in by boat over the sea. How much sulfur should the contract call for, over the year, the yield being taken as stated in the text?

2. A plant manager finds that there are produced in his chamber plant 40 tons of 50° Bé. sulfuric acid every day. It would be better for his sales opportunities if that acid could be strengthened to 66° Bé. acid. Could a contact plant be erected which might take the weak acid and raise its strength to the desired one? How much sulfur would be required per day?

3. The reaction heat in the converter is 45.2 Calories for $2\text{SO}_2 + \text{O}_2 = 2\text{SO}_3$. Compute the total heat in Btu. for a plant making 40 tons of 100 per cent H_2SO_4 per day. Conversion factors will be found in the appendix. Compare the number of pounds of bituminous coal which would generate the same amount of heat. (*See Chapter 12 for the fuel value of coal.*)

4. Make the same comparison of heats for the amount of sulfur burnt in the plant specified in Problem 13, if the heat evolved is $\text{S} + \text{O}_2 = \text{SO}_2 + 69$ Calories, and the equivalent weight of bituminous coal.

5. An 86.3 per cent total SO_3 oleum may be said to be 105.8 per cent H_2SO_4 , because it can be extended by the addition of water, at least theoretically, to give 105.8 parts of such acid. It is not done actually, because the reaction with water is violent; the dilution is by means of a weaker sulfuric acid. Given the same oleum, find the amount of free SO_3 , and of the amount of 100 per cent H_2SO_4 it contains.

Method: 86.3 per cent oleum contains 13.7 per cent water, hence $13.7 \times 98 \div 18$ parts of H_2SO_4 . The corresponding amount of sulfur trioxide is bound and the remainder is free.

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Until recent years, the only commercial way to make nitric acid was with the aid of the non-volatile sulfuric acid, liberating the volatile nitric acid from its sodium salt. Nitric acid is now made from atmospheric nitrogen, via ammonia. Its production from natural nitrates died out for some years, at least in the United States; it may be coming back because of war demands. From whichever source it is obtained, nitric acid is irreplaceable in the manufacture of dye intermediates and explosives. In peace time, nitrogen compounds are of the greatest importance for agriculture.

Chapter 2

Nitric Acid, Chile Saltpeter, Mixed Acid, Iodine, Hydrofluoric Acid, Aluminum Sulfate

Until about 12 years ago, nitric acid was made exclusively by the action of sulfuric acid on Chile saltpeter, the commercial salt of the acid. Since then, the manufacture of nitric acid by the catalytic oxidation of ammonia with atmospheric oxygen, described in full in Chapter 6, has become the standard process. A number of plants continued nevertheless to make their nitric acid from sodium nitrate and sulfuric acid, in the usual retorts, because in that way the concentrated acid, 98 and 99 per cent HNO_3 , is readily obtained, while the oxidation of ammonia furnishes 50 or 60 per cent nitric acid at best. The strong acid is indispensable for the manufacture of explosives, of dye intermediates, and for most nitrations. The weaker acid may be concentrated by mixing it with sulfuric acid and then distilling; another way is to neutralize the weaker acid with soda ash, isolate the sodium nitrate formed, and treat it in retorts with sulfuric acid. The second method has the advantage of producing a by-product, nitre cake, which becomes the starting material for a number of other heavy chemicals, all of them indispensable in the national economy.

For decades Chile saltpeter was an essential material for the chemical industries; but early in the thirties, it had lost much of its earlier importance. From the earliest day of its production to the present, its main use was and still is as a nitrogenous fertilizer; on the basis of tonnage, its service as a raw material for nitric acid manufacture was secondary. A part, but only a part, of the tremendous decline was due to the world depression. Chile saltpeter lost in importance mainly because synthetic ammonium sulfate, and soon synthetic sodium nitrate, largely replaced it in world markets. In the year June 1928-June 1929, Chile saltpeter equivalent to 490,000 metric tons of nitrogen was produced; from that date on, the production declined, reaching a low of 71,000 in 1932-33. Since then, the amount produced has been rising. In 1935-36, it was 192,000 metric tons of nitrogen; in the next year, 205,000 tons, and in 1937-38, 22,500 tons. The moderate rise in production results from unusual demands by the nations in a troubled world, and was helped by the introduction of an improved system for extraction of the nitrate from the ore. At the present time (1942) conflicting forces are influencing the production.

Chile saltpeter is extracted from an ore found in the Terapaca and Arica



districts in northern Chile, where the rainfall is so scant that the soluble salts present in the soil have not been washed away. The nitrate-bearing rock lies near the surface, under 6 to 10 feet of overburden, and extends to a depth of 50 feet. The Shanks method of extraction, the older method, is to load the rock, called "caliche" if rich, and "costra" if poor in nitrates, into carts or cars. These are pulled to the plant by mules; there the ore is crushed to a coarse size, loaded into leaching tanks and treated with hot water. A series of tanks is employed, and the extraction is counter-current, so that a strong, hot solution is obtained from which the nitrate crystallizes on cooling. Sodium nitrate is extremely soluble in water. During the leaching, the slightly soluble sulfate is left behind with the insoluble earthy portions, and also some of the other salts present in the ore, as indicated in Table 4a.

TABLE 4a.—*Analysis of a typical caliche.*

Sodium nitrate	17.6%	Magnesium sulfate	3.9%
Potassium nitrate	1.3	Calcium sulfate	5.5
Sodium chloride	16.1	Sodium iodate	0.11
Sodium sulfate	6.5	Sodium borate	0.94
	Potassium perchlorate	0.23	

Total salts 52.18%.

A certain amount of sodium chloride and other salts pass into the nitrate liquor; part of these crystallize with the nitrate, and part remain in the mother liquor.

In the newer Guggenheim process, the extraction is performed at 40° C. (104° F.), instead of steam temperatures. Mining and hauling to the extraction plant are performed by power shovels and cars; the ore is freed of earthy admixtures (as fines which pass out) on vibratory screens, and is then leached in an elaborate series of tanks by spent mother liquor at the temperature mentioned above. The rich nitrate liquor is cooled to 15° C. (59° F.) in interchangers against outgoing spent liquor, then to 5° C. (41° F.) by ammonia refrigeration. Sodium nitrate crystals separate to some extent in intermediate vessels with cone bottoms; most of the crystals remain suspended, and are thickened in mechanical thickeners. The slurries of crystals are centrifuged; the crystal mass is then briquetted, heated to melting in a reverberatory furnace, and the melt sprayed from nozzles to form pellets. The greater part of the mother liquor, after passing the interchangers, is used again; part of it is worked up for its iodate and potassium nitrate content. The Guggenheim system employs mechanical methods in mining and loading, and the operations in the plant are highly mechanized, so that the labor cost is low; it requires less fuel, works poor as well as rich ores, and gives a product analyzing 98.8 per cent NaNO_3 , against 95.5 per cent for the Shanks product. The pellets are shipped in bulk or in packages. The Shanks nitrate is shipped mostly in burlap bags.

A considerable amount of Chile saltpeter is used in dynamite mixtures, as such, without any treatment.

The production of Chilean sodium nitrate in the season 1939-40 was 1,639,835 short tons, and the price \$29.00 to \$29.40 a ton. In the preceding year, the production was 1,573,074 short tons.

NITRIC ACID FROM SYNTHETIC SODIUM NITRATE

The reaction between sulfuric acid and sodium nitrate takes place in cast-iron retorts varying in capacity between 1500 and 5000 pounds. The nitrate is shoveled in through an opening in the front of the smaller, cylindrical retorts, or dumped into the larger, square or pot-type retorts through an opening in the top, from small trucks on rails. The sulfuric acid is run in next, and then the retort is heated gently from its own small fireplace. Nitric acid is a liquid which boils at 86° C., so that it is readily vaporized; high heat is detrimental, for it decomposes the acid. The vapors pass to a condenser cooled by water; the gases which do not condense are absorbed in water in final towers called Lunge towers. The operation of the retorts is intermittent, and for any size requires one day when working normally.

The amount of sulfuric acid is sufficient to form the acid sulfate, $\text{NaNO}_3 + \text{H}_2\text{SO}_4 \rightarrow \text{HNO}_3 + \text{NaHSO}_4$; only one-half of this acid functions to liberate nitric acid, the other half remains unused. The reason for this practice is that the acid sulfate is a liquid and may be run out. Its acid content is fully utilized in the normal sequence of heavy chemical manufacture.

The amount of acid in the acid sulfate, called the nitre cake, is not 40.80 per cent, as the formula NaHSO_4 suggests, but 37.33, or even 30 per cent; the amounts of water vary, with a corresponding variation in the melting point, which lies between 210 and 320° F. (99° and 160° C.).¹ At the beginning of the distillation the strongest acid passes out, essentially anhydrous; near the end, a weaker acid is produced as the temperature is raised. The aim of the nitric acid maker is to produce strong acid; a certain amount of weak acid is unavoidable, for on decomposing, nitric acid itself produces water; but the amount of weak acid may be considerably reduced by using strong sulfuric acid. 98 per cent H_2SO_4 , in the retort instead of the more usual 66 Bé. acid. The acid is more or less brown in color, especially the concentrated acid, because of the presence of oxides of nitrogen.

The condensation of the vapors is performed chiefly in one of two systems, the Gutmann system and the S-bend or Skoglund system. Other installations are the Hough, the Valentiner and the Uebel. The Gutmann system is illustrated in Figure 17.

Bleached Nitric Acid. It is necessary, for certain uses, to produce nitric acid free or almost free from the lower oxides of nitrogen (such as NO , NO_2). A pale nitric acid of this type is produced by the Valentiner system which includes operation under reduced pressure (one-third atmosphere); an easier way is to set up a bleacher in connection with an S-bend condenser, and operating at normal pressure; this constitutes the Skoglund system. The bleacher consists of a Duriron (or stoneware) tower about 10 feet high and 30 inches wide, set immediately behind the retort and below the condenser. The condensed acid flows down the tower, and the hot gases travel up, removing nitric oxide and dioxide from the liquid; the acid leav-

¹ Some further remarks on this matter will be found in Chapter 3.

ing the base of the bleacher is cooled by passing through a U-shaped tube set in cold water; from here it flows to the receiver. Most of the lower oxides of nitrogen reach the Lunge towers.

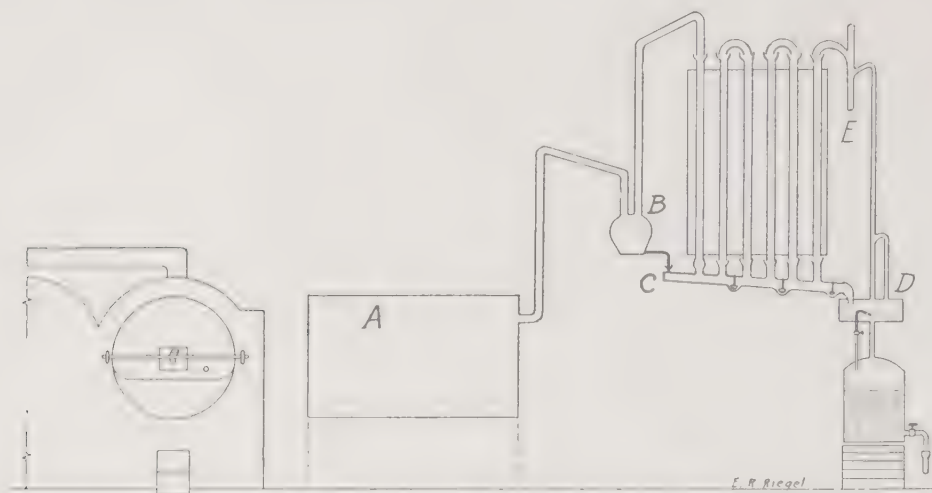


FIGURE 17.—Nitric acid from nitrates with the Gutmann condensing system. A, retort; B, collector for air-condensed acid; C, chamber pipe with water-cooled pipes; D, separator and receiver; E, connection to Lunge tower and chimney.

The bleacher just described serves well for strong acid, such as 98 per cent HNO_3 , which usually is to be made into "mixed acid." It is sometimes desired to bleach a weaker acid, with the special purpose of making it chlorine-free. This may be done by adjusting the strength of the acid to 42° Bé. at 60° F. or 15.5° C. (67.18 per cent HNO_3), placing it in a stoneware pot set in warm water, and blowing in compressed air filtered through glass wool. A white acid results; it is suitable for manufacturers of jewelry who wish to recover gold from its copper and other alloys; it must contain no chlorine, for this would cause a loss of gold. Nitric acid made by ammonia oxidation, or from synthetic sodium nitrate, is free from chlorine.

Gas Recovery Towers. The lower oxides of nitrogen escape condensation when merely cooled; recovery towers are therefore provided in which such gases meet a trickle of water; at the same time they are oxidized, at least to a considerable extent, so that the amount of nitrous acid decreases, while that of nitric acid increases. The gas usually carries enough air for this oxidation. The original examples designed by George Lunge have almost flat plates with perforations and ridges, so that each plate retains a certain amount of liquid, which is replaced as the liquid from above reaches it; the gas enters at the base, the water at the top. Solution of the gas takes place at each level. The strongest gas meets the rather strong solution (40 per cent HNO_3) near the base, and can enrich it somewhat; after rising to near the top, nearly exhausted, its remaining contents are abstracted by the water, as yet uncharged with acid. This tower exemplifies the counter-current principle.

The Hough system is even more compact than the Gutmann; it is made

of Duriron. The Gutmann system is nearly always stoneware; the Skoglund usually has stoneware cooling pipes, which may be replaced by Duriron or silica. The Valentiner system has stoneware coils hung on a stoneware frame, these are more expensive than the simple S-bends of the Skoglund and the straight pipes of the Gutmann, so that a break is a more serious matter. The Uebel system employs three retorts working in series, and is designed for the use of weak sulfuric acid.

The specific gravities for the various strengths of nitric acid increase steadily, but more slowly, at the higher strengths, than the concentration.

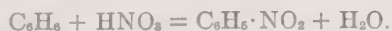
	° Bé.	Sp. Gr.	Per Cent HNO ₃
Nitric acid (15° C/4° C).....	36	1.33	52.34
"	40	1.38	61.24
"	45	1.45	77.24
"	47	1.48	86.01
"	49	1.51	98.05
"	49.63	1.52	99.62
"	49.654	1.5204	99.70

One hundred per cent nitric acid exists only as a solid at -41.3°C . (-42.3°F .); a certain amount of decomposition into the anhydride and water takes place on melting. Above 45°Bé , the acid is generally yellow to brown.

Nitric acid and water forms a constant boiling mixture with maximum boiling point, at 120.5°C . (249°F .), containing 68 per cent HNO₃. On distilling a commercial acid for purification, this is the acid obtained; this has therefore become the standard strength for "C.P." acid. It is water-white. 122,596 tons of 100 per cent nitric acid were produced in 1935 in the United States, from synthetic sodium nitrate, valued at \$89 a ton, or 4.5 cents a pound; in 1937, 175,860 tons, of which 140,450 tons were made and used in the same establishments, and 35,410 tons sold, at \$86.2 a ton. In 1939, a total of 167,740 tons was made, of which 133,169 were made and used in the same establishments, while 34,571 tons were sold at \$92.0 a ton. A far greater amount will be manufactured during the present war.

MIXED ACID

In any nitration, as for instance in that of benzene, two products result: the nitrated body, here nitrobenzene, and water; as the reaction proceeds the water accumulates and tends to reverse the action. To prevent this, concentrated sulfuric acid is added; it binds the water, and permits the nitration to proceed to completion:



It has become customary to mix the nitric and sulfuric acids at the factory, before shipment to the consumer; this saves him one operation, and the mixture may be shipped in steel tank cars, as sulfuric acid is shipped, whereas nitric acid is usually shipped in glass. The mixture of the two acids is called "mixed acid"; it varies in the relative proportions of nitric and sulfuric acid it contains, and also in its water content, and is made to order.

Examples:

Nitration of wood pulp for "fibre".....	45.0% HNO ₃ ;	48.0% H ₂ SO ₄
Nitration of benzene	30.0	54.0
For nitroglycerin	35.6	58.0

To make mixed acid, nitric acid is raised by means of a stoneware elevator with stoneware ball valves to a upper level, and from there is fed by gravity to the mixing vessel, at about the same rate as the sulfuric acid. The mixing vessel may be a cylindrical steel tub with a paddle. Heat is evolved, which is dissipated during the slow mixing and on standing over night. In the newer plants, the mixing room is placed at a lower level than the nitric building, so that the nitric acid may be fed by gravity. The mixing is made more rapid by circulating the acid from a steel storage tank through a condenser cooled by water, and feeding the nitric acid gradually into the tank containing the charge of sulfuric acid. The circulating pump is a small steel centrifugal pump; it draws the acid from the bottom of the tank and delivers it at the top on the opposite side. The same storage tank serves as an acid egg for loading the railway tank car, which it equals in size.

Mixed acid is almost colorless.

The production of mixed acid in 1935 was 46,074 tons, valued at \$45.50 a ton; in 1937, the production was 54,432 tons, sold at \$45.75 a ton; in 1939, 56,517 tons, sold at \$47.70 a ton.

IODINE

Until 1931, the world production of iodine was about 2 million pounds a year, and nearly all of it was made from the mother liquor of Chilean nitrate; the price was \$4, then \$3 a pound. Since that date, the prospect of the complete closing down of the Chilean fields has caused a search for other sources of iodine;² this has been successful, and the monopoly of the Chilean producers has been broken. The domestic production was 245,696 pounds, while the imports, all from Chile, were 375,819 pounds, priced at \$1.12 a pound. The price in 1935, in the United States, for domestic iodine, was \$1.05 a pound; the year before, it had been \$1.23.

The possible production per year from a variety of sources other than Chilean nitrate is:

	Tons	Source
Europe	140	Seaweed
Japan	150	Seaweed
Java	80	Artesian wells
United States	500	Oil wells (brines)
Russia	240	Seaweed and oil wells
Total	1110	

The iodine is present chiefly as iodide; the average concentration in brines is low (equivalent to 0.05 gram per liter), so that efficient and well-conceived processes must be installed.^{2a}

On the other hand it is estimated that if 500,000 tons of Chilean nitrates are produced, which is one-fifth of the normal sales, enough iodine for the world's consumption could be produced at a cost of about 50 cents a pound. The method would be the one used in the past: The mother liquor from the

² "Fortunes and misfortunes of iodine," by P. F. Holstein, *Chem. Met. Eng.*, 39, 422 (1932).

^{2a} U. S. Patent 1,944,423; 2,009,956.

Chile saltpeter crystallization contains 5 grams of iodine per liter in the form of calcium iodo-chromate, calcium iodate, and some sodium iodate. The free iodine is liberated by addition of sodium bisulfite solution, in the form of a solid which sinks to the bottom of the tub.³ It is flushed into canvas bags, washed with water several times, and pressed to a cake by means of a hand press. This crude product is then distilled from cement-lined iron retorts, heated by a coal fire; stoneware pipes are fitted to each retort and in these the iodine deposits in the form of crystals containing 99 per cent or more of iodine; the moisture in the cake escapes through the loose joints in the condensing pipes. The crystals are packed in barrels holding 120 pounds, and these are wrapped in cow hides, which on shrinking form an air-tight cover which prevents the loss of iodine by sublimation. The reaction is



Iodine forms black, flat crystals, soluble in alcohol to a brown solution, the tincture of iodine used in the pharmacy. It serves also for the manufacture of iodoform, of aristol (di-thymol-di-iodide) its improved substitute, and of sodium and potassium iodide. It is used by the chemical analyst, in chemical laboratories in general, and for the manufacture of a few dyes; it is also used in iodized salt for table use.

The production of iodine resublimed in the United States in 1939 was 404,344 pounds, valued at \$1.13 a pound.

HYDROFLUORIC ACID

Hydrogen fluoride (HF, or more correctly, H_2F_2) is a gas which is extremely soluble in water; this water solution is termed hydrofluoric acid. Hydrogen fluoride is made by the action of sulfuric acid on calcium fluoride (CaF_2) which occurs as the mineral fluorspar in Illinois and Kentucky in the United States, and in England and other countries. The original method consisted of batch distillations from small two-piece lead retorts; this has been displaced by continuous methods, of which the following is an example.⁴

A cast-iron retort 12 feet long and 3 feet in diameter is rotated at a slow rate and heated from the outside by fire gases. At the charging end *A* (Fig. 18) a mixture of powdered fluorspar and sulfuric acid of various strengths is fed in through a stationary disk, fitting by means of a sleeve into the rotating cylinder. A slight inclination causes the mass to move forward until it finally reaches the discharging end *B*. The gas and moisture pass out through the opening in the stationary disk and are condensed in a lead coil. The temperature at the charging end is 120°C ., at the discharging end 320°C .

The gas passes down a lead coil laid in water into a receiver, which has a charge of water and is surmounted by a small lead tower containing wetted lead trays. The amount of water is regulated to produce the desired strength.

The operation is not quite continuous, for the charging must be done at frequent intervals (30 minutes); the reason is that the mixed fluorspar and

³ "The production of iodine in Chile" John B. Faust, *Ind. Eng. Chem.*, 18, 808 (1926).

⁴ German Patent 262,505 (1913), to H. B. Bishop, of Brooklyn, N. Y.

acid tend to set to a hard mass which gives off fumes of hydrogen fluoride after a few minutes. The practice is to mix the acid and mineral in small batches for 30 seconds, and introduce all of it into the retort before it can set; the evolution of the gas in the retort is fairly even. The roasted solid collects in the front end and is discharged periodically. The cylinder rotates about once in 20 seconds.

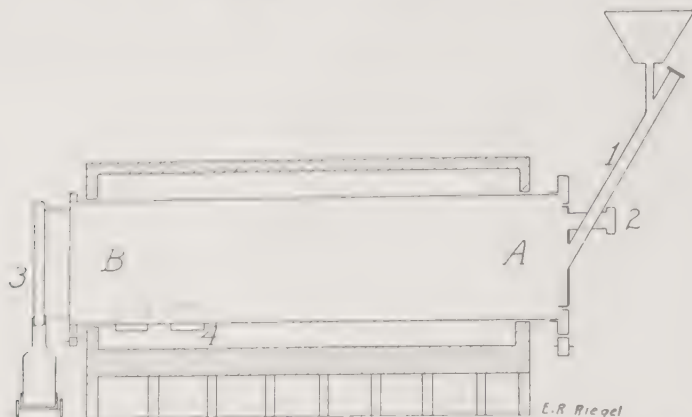


FIGURE 18.—Retort for the continuous generation of hydrofluoric acid; 1, charging pipe; 2, outlet for gas; 3, discharge ring for calcium sulfate; 4, outlet of fire gases to the flue. The retort rotates; 1 and 2 are part of the stationary disk.

Another continuous method is that of the Rhenania Company,⁵ in which sulfuric acid, as oleum, is absorbed in anhydrous calcium sulfate; with one-half its weight of acid the calcium sulfate is still a solid. This is mixed with finely pulverized calcium fluoride, and the resulting mixed dry charge may be fed to a muffle with mechanical plows, such as the Mannheim furnace;⁶ hydrogen fluoride is evolved as a gas and dissolved in water, using lead or platinum vessels, while the roasted solid is discharged continuously and, in part, used over again. In still another proposal,⁷ a great excess of nitre cake replaces the sulfuric acid.

The reaction in the case of 99 per cent H_2SO_4 , as the Bishop patent recommends, is $\text{CaF}_2 + \text{H}_2\text{SO}_4 \rightarrow \text{CaSO}_4 + 2\text{HF}$. Any moisture passing over with the gas condenses in the cooling coil and remains in the acid solution. The usual commercial strengths are 30 per cent and 60 per cent HF; the 30 per cent acid is shipped in tight oak barrels, paraffin-lined; the 60 per cent acid in rectangular lead carboys 8 by 12 by 18 in., protected by a wooden box. A certain amount of the crude acid is redistilled from lead stills and shipped in ceresin wax⁸ containers containing 1 pound or less. The pure acid is colorless; its action on the skin is extremely painful and lasts many hours.

The chief uses of hydrofluoric acid are for making fluorides, for cleaning stone, and for etching glass. Mixed with sulfuric acid it serves to remove the dull surface left by the grinding tool in cutting "decorated" glassware.

⁵ German Patent 355,524.

⁶ Chapter 3.

⁷ German Patent 306,567.

⁸ Chapter 24.

The fluoride of sodium is made by neutralizing the acid by soda ash. Ammonium fluoride may be made similarly, or directly by heating together ammonium sulfate and calcium fluoride, when the ammonium fluoride sublimes and collects on the cooled cover of the retort.⁹

In 1939, 4,345,609 pounds of hydrofluoric acid as 100 per cent HF were produced, valued at 15.25 cents a pound.

Fluosilicic acid may be made by the action of hydrofluoric acid on silica: $6\text{HF} + \text{SiO}_2 \rightarrow \text{H}_2\text{SiF}_6 + 2\text{H}_2\text{O}$. On a large scale, it is a by-product of calcium superphosphate manufacture,¹⁰ in which the sulfuric acid with the fluoride impurity in the phosphate gives hydrofluoric acid gas, which reacts in part with the silica impurity giving silicon fluoride, SiF_4 ; the two escaping together are dissolved as a weak solution (10° Bé.) of fluosilicic acid. This may be concentrated to 13 per cent H_2SiF_6 , beyond which strength decomposition occurs, with loss of SiF_4 . By adding soda ash, the sodium fluosilicate is made and may be concentrated to dryness; by adding magnesium hydroxide or carbonate, magnesium fluosilicate, MgSiF_6 , of great importance to the cement industry, is obtained. Fluosilicic acid and its salts are insecticides.

In 1931, the production (U. S.) of fluosilicic acid was 3,734,000 pounds, and the price under 2 cents a pound.

Calcium fluoride may be made directly into silicon fluoride by heating it with silica in a rotating oven in the presence of magnesium sulfate; the silicon fluoride may be absorbed in a salt (NaCl) solution with the formation of sodium fluosilicate.¹¹

Hydrofluoric acid is injurious to workmen; great care must be exercised in using it; rubber gloves and good ventilation must be provided.

ALUMINUM SULFATE

Aluminum sulfate is an important heavy chemical; it is used in paper making, in the textile industry, as a mordant for certain dyes, in the purification of river water for municipalities, and for a number of other purposes. The production (U. S.) of aluminum sulfate (filter alum) was: 1937, 393,411 tons valued at \$22.75 a ton; in 1939, 416,108 tons valued at \$20.30 a ton. "Filter alum" is the cheapest grade of aluminum sulfate.

Aluminum sulfate is made by dissolving finely powdered bauxite, a naturally occurring hydrated alumina ($\text{Al}_2\text{O}_3 \cdot x\text{H}_2\text{O}$), obtained from southern France, or from Arkansas, Tennessee, and other countries [see table of production in Chapter 18], in sulfuric acid of about 50° Bé. (62 per cent H_2SO_4), to which washings from previous batches have been added.



Several bauxite analyses follow:

	Al_2O_3	SiO_2	Fe_2O_3	Ignition Loss
Red bauxite (French)	58-60%	3- 3.5%	1-20%	20-25%
White bauxite	50-72	6-23	1- 9	20-22
Gray bauxite	56-61	7-15	1-14	21-25

Bauxite contains titanium, from a trace to 4 per cent TiO_2 ; it may also contain selenium.

⁹ German Patent 94,849.

¹⁰ Chapter 7.

¹¹ German Patent 319,559.

The dissolver is lead-lined, and is provided with steam coils and a cast-lead propeller. The strong solution obtained is run to a larger tank and diluted with water sufficiently to give good settling of the undissolved matter. After settling, the clear solution is decanted, or filtered in wooden plate-and-frame presses; the bottom mud or press cake is washed with water, and the washings used in the next batch. In this diluting tank also, before running off the clear liquor, the iron salts are reduced by sodium sulfide, sodium bisulfite, or sulfur dioxide gas, from the brown-colored salts to the nearly colorless ferrous salts; they are not removed, but remain in the alum cake as ferrous salts.

The clear solution, with its iron reduced, is concentrated in a boiler until its content of alumina is 16 per cent Al_2O_3 ¹²; the solution is then run out into flat floor pans (steel) and let stand over night. In the morning the pan content is solidified to a white cake, with no sign of crystallization; the cake is broken by bar and chisel, reduced in a hammer mill¹³ followed by a cage disintegrator¹³ to a coarse powder, and barreled. The floor pans are usually 20 feet by 38 feet by 4 inches deep. In the newer plants, the pans are made a little smaller and set on a hinge so that they may be tipped when ready to dump; a hammer strikes a blow on the under side of the pan automatically when it reaches the proper dumping angle. The fractured cake drops off by gravity into a screw conveyor which feeds the hammer mill.

The preliminary treatment of the bauxite rock consists of crushing in a swing hammer mill,¹³ followed by pulverization in a Raymond suction mill.¹³

Sodic Aluminum Sulfate. One method for making sodic aluminum sulfate, $\text{Na}_2\text{SO}_4 \cdot \text{Al}_2(\text{SO}_4)_3$, is to add nitre cake to aluminum sulfate solution, purifying from lead and arsenic (by H_2S), and concentrating in lead pans; as long as the liquor is 32° Bé., not weaker, the lead from the pan is not dissolved. Concentration proceeds until the cooled mass gives a hard cake, which is crushed. All the water and most of the acid are removed in a rotary roaster, yielding a mass made up of particles the size of peas. This material is milled in a Raymond mill, and forms a very fluffy white powder, used in baking powders. On dissolving in water, it must give an acid action with bicarbonate.

The production of sodic aluminum sulfate in 1935 was 18,359 tons, at \$55.50 a ton.

Potassium alum, $\text{K}_2\text{SO}_4 \cdot \text{Al}_2(\text{SO}_4)_3 \cdot 24\text{H}_2\text{O}$, is made by adding potassium sulfate solution to aluminum sulfate solution, concentrating, and letting cool and harden in crystallizers with removable sides; a small amount of mother liquor flows off the crystals, which are otherwise ready for shipment.

Ammonia alum is also produced regularly; the 1939 production was 5,065 tons, valued at \$53.50 per ton.

Oxalic acid, $\text{H}_2\text{C}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$, a crystal, is made in various ways; one of them is by the action of nitric acid on glucose from starch, in the presence of sulfuric acid. The reaction is



¹² Crystallized aluminum sulfate, $\text{Al}_2(\text{SO}_4)_3 \cdot 18\text{H}_2\text{O}$, contains 17.35% Al_2O_3 .

¹³ Chapter 44.

which is made to proceed at 165° F. (73.89° C.). The oxalic acid is crystallized from the 20 per cent solution, which also contains sulfuric acid 44° Bé. The starch is hydrolyzed in a preliminary operation. In 1939, the production of oxalic acid in crystal form was 8,265,490 pounds, valued at 10.5 cents a pound.

PROBLEMS

1. It is required to produce every working day 18,000 pounds of 98.05 per cent nitric acid, from sodium nitrate containing 98 per cent NaNO_3 , the yield to be 90 per cent. How much sodium nitrate will be required per day, at least theoretically? This charge must be divided evenly between 10 retorts, each receiving one charge per day.

2. In Problem 1, how many pounds of 66° Bé. sulfuric acid (93.19 per cent H_2SO_4) will be required for changing all the nitrate into nitric acid? To make certain that no unwanted water will come from the sulfuric acid, it is later decided to use 98 per cent acid; in that case, how many pounds will be required?

3. Due to the decomposition of part of the nitric acid, water is formed, and only part of the yield is in the form of the desired strong acid. If for problem 1, 70 per cent of the recovered acid is in the form of 98.05 per cent HNO_3 , the remainder in the form of weaker acid which must be marketed separately, how much nitrate and acid will have to be used?

4. The specific gravity of the 66° Bé. sulfuric acid in Problem 2 is 1.835; the amount required is measured in an elevated lead-lined box, one box for each retort, of which there are 10. The box is 2.5 feet \times 2.5 feet, and 54 inches deep. To what height in the box (dipped with a lead stick) must the box be filled to provide the necessary amount of sulfuric acid? Weigh tanks are now being used rather than dip tanks.

5. In Problem 4, what is the weight of nitre cake furnished by the 10 retorts per day? The nitre cake will contain all sulfate radical introduced by the acid, all the sodium radical brought by the nitrate, and such water as the sulfuric acid brought. The sodium nitrate should be considered anhydrous.

6. The sales department calls for 2,750 pounds of 60 per cent hydrofluoric acid per day. How many pounds of calcium fluoride must be taken, if the yield is 92 per cent, and if the calcium fluoride rock contains 90 per cent CaF_2 ?

7. In Problem 6, how many pounds of 66° Bé. sulfuric acid will be required?

8. The mother liquor from a Chile saltpeter crystallization is to be worked up for iodine. It contains 9.5 grams of calcium iodate per liter, and there are 28,315 liters available. How many pounds of iodine will be obtained, the yield being 89 per cent?

9. A manufacturer converts 1,000 tons of bauxine every year, containing 58 per cent alumina of which 56 per cent enter the final product, into aluminum sulfate containing "16 per cent Al_2O_3 ." On the alumina in the bauxite which is consumed, the yield may be considered 100 per cent. How many tons per year does he produce? How many tons for each day of a 300-day year?

10. A mixed acid is to contain 46.0 per cent HNO_3 and 46.6 per cent H_2SO_4 . There is available a 49.5° Bé. nitric acid, containing 92.03 per cent HNO_3 . What strength sulfuric acid will be selected, and how many pounds by weight of each will be required to make 10 tons of the mixed acid? There are shipped every week two tank cars of this mixed acid, weighing 100,000 pounds net each. How much nitric acid of the strength indicated will be required over the week, and for six working days, how many must be produced every day?

OTHER PATENTS

U. S. Patents: 1,998,196, nitric acid manufacture; 2,018,397, anhydrous hydrogen fluoride; 2,055,283; sodium aluminum sulfate, improved method of manufacture; 1,944,123, recovery of iodine from the adsorbing charcoal; 1,998,014, iodine recovered from impure silver iodide; 2,009,956, iodine extracted from natural brines; 2,212,135, production of nitric acid by compressing lower oxides of nitrogen and other steps; Can. Pat. 386,477, on concentrating nitric acid; U. S. Patent 2,189,363.

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"New American iodine industry," G. Ross Robertson, *Ind. Eng. Chem.*, 26, 376 (1934).

In the course of manufacture of soda ash by the old Leblanc process, there was discharged into the atmosphere a steady stream of hydrogen chloride; on misty days, the neighborhood of such a plant was shrouded in a fog. Laws were passed, such as the Alkali Act in England (1863) which forbade the discharge of such concentrated gases. It became necessary for manufacturers to erect absorbing towers, in which the gas was absorbed in water. The solution so obtained was the first commercial hydrochloric acid, then called *muratic acid*, and became an important "heavy chemical." Hydrochloric acid is the first example of a waste product which has been saved and changed into a useful one.*

Chapter 3

Salt, Soda Ash, Salt Cake, Hydrochloric Acid, Glauber Salt, Sodium Silicate, Bromine

Salt (NaCl) occurs in nature in almost unlimited quantities. It is the direct source of such sodium compounds as soda ash, caustic soda, sodium sulfate or salt cake, crystallized sodium sulfate or Glauber salt; indirectly, through soda ash, it furnishes the sodium for sodium phosphate and many other salts. Moreover it is the source of chlorine and of hydrochloric acid. It is the uses above which come to the chemist's mind when he thinks of salt; but even without these it has an imposing list of uses, which place it among the important substances in the economic world. It serves to preserve meat, fish, and hides; it is a necessary article of diet, and as such appears on every table; it is used in dairies to give temperatures below the ice point; and it is used to thaw out switches in winter. Salt enables the soap maker to separate the soap from the glycerin lye, and the dye manufacturer to precipitate his products; in addition, salt is one of the important water-softening agents.

The form of salt used in nearly all the chemical industries,¹ in the northern part of the United States at any rate, is rock salt, cut from the solid salt deposit by means of a shaft. There are only a few shaft mines; three well-known ones are at Retsof, Livingston County, New York; at Myers, Tompkins County, New York; and near Detroit, Michigan. These shafts are 1073, 1950 and 1133 feet deep, respectively. There are shaft mines in Kansas (4), in Louisiana (4), and in Texas (2). The rock salt is lifted to the mouth of the shaft, crushed and screened to size, without any other operation for purification. The color is a light grey-white, and it is essentially pure (98.5 per cent NaCl). At Avery Island, Louisiana, the salt dome reaches the surface, and rock salt is mined as in shaft mines. The quality usually runs 99.4 per cent NaCl . The production of rock salt by states is given in Table 5. In 1935, New York, Louisiana, Kansas and Michigan together produced 93 per cent of the total rock salt mined. In 1940, rock salt was produced in Kansas, New York, Louisiana, Michigan, New Mexico, Texas, Utah, California, and Colorado.

* Another Act in 1874, prescribed that the discharge gas must not contain more than 0.0648 gram of HCl per cubic foot.

¹ Except soda ash, for which the brine is better adapted.

TABLE 5.—*Production of Rock Salt by States in 1931.**

(Bureau of Mines, "Mineral Resources of the United States," 1931, part II.)

	Tons		Tons
Michigan	787,040	California	310,360
New York	350,410	West Virginia	35,480
Ohio	319,450	Undistributed	130,290

* Since 1931, rock salt produced is no longer listed by states.

Salt is obtained more frequently by means of water sent down one pipe, and after becoming saturated, brought up by another pipe concentric with the first (partly by hydrostatic pressure), and then pumped to a refining plant. Such artificial brines permit a cheaper operating cost, and are well adapted to soda ash manufacture and particularly to the making of white table salt. Artificial brines are obtained in New York State at Watkins Glen, Silver Springs, Myers, and Tully near Syracuse. Artificial brines are made in Michigan, where natural brines also occur but are of less importance; one field is near Detroit (Wyandotte) and a second one in the center of the State, near Midland. Kansas has many artificial brine wells; West Virginia uses chiefly natural brines; Ohio both. A number of other states produce artificial brines.

In the dry climate of the western states, salt is found as an outcrop at the surface;² in some of these states this salt is utilized to some extent.

In southern California, as also in Spain and southern France, sea water is concentrated in wide basins, by solar evaporation, until the salt deposits; by running off the mother liquors at that point, the bitter magnesium salts are removed. An interesting application of the same method is at Salt Lake, Utah. Of the many salt deposits of the world, those at Stassfurt, Germany, underlying the potassium salt beds, deserve mention because they are several thousand feet thick. The bed at Retsof, New York, is 8 feet thick; the stoutest bed in America is one in Kansas, 400 feet thick,³ while a Texas salt dome is said to be 3000 feet thick.

From the brines, whether artificial or natural, a grade of salt suitable for table and dairy use is made by solar evaporation (in sunny climates), by open-pan evaporation, or by evaporation in vacuum pans, with one pan (single effect) or several pans (double or triple effect); in the latter the steam raised from the salt solution in one pan becomes the heating steam in the next pan.⁴ The evaporation of salt solutions offers the difficulty that, as salt is about as soluble in cold as in hot water, cooling a hot strong solution is not enough to form crystals; the water must actually be removed from the hot solution, until the salt drops out for lack of solvent.

The precipitated salt is dried in rotary driers, frequently constructed of Monel metal.

There were 83 plants of 66 companies operating in 1940; 60 plants produced evaporated salt, 22 produced rock salt, 10 produced salt in brine. Pressed blocks were made by 19 evaporated salt plants and 8 rock-salt plants. The several states in the production of salt in any form stand as fol-

² From the streets of the town of Salina, Sevier County, Utah, outcrops of salt may be seen at the side of the hills; its color is red, and it may be fed to cattle.

³ "Technology of salt making in the United States," W. C. Phalen, *Dept. Interior Bull.* No. 146

1917, p. 124.

⁴ Chapter 43.

TABLE 6.—United States Salt Production in Short Tons.*

	1939		1940	
Salt from all sources.....	9,277,911	\$2.64	10,003,448	\$2.61
Evaporated salt.....				
Open pans or grainers.....	499,331	8.59	505,491	8.41
Vacuum pans	1,615,838	5.85	1,667,273	5.82
Solar	391,287	3.57	457,710	3.57
Pressed blocks, evaporated salt...	152,121	7.45	152,267	7.81
Rock salt.....				
Bulk	1,995,915	3.12	2,225,377	3.15
Pressed blocks	39,242	6.71	40,171	7.03
Salt in brine	4,584,177	0.40	4,955,159	0.383

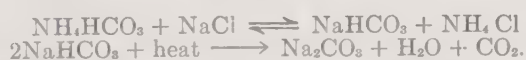
* Minerals Yearbook, 1940.

lows, the first with highest production, the others in the order of decreasing production: Michigan, New York, Ohio, Louisiana, Kansas, California, Texas, and New Mexico. Puerto Rico produced a little less salt than New Mexico.

SODA ASH, THE COMMERCIAL SODIUM CARBONATE

In the United States, soda ash from salt is made by the ammonia process exclusively; in England, a certain amount, decreasing yearly, is made by the older Leblanc process; but even there, over three-quarters of the total production is by the ammonia process. In France, Belgium, Germany,⁵ and other countries, the soda ash made is ammonia soda. To some extent, natural soda is isolated from the accompanying salts; such natural sodas and the ashes of seashore plants were the only source until Leblanc invented his process in the closing years of the eighteenth century.

The ammonia soda is usually called Solvay soda, for the successful manufacture, in 1864, by this process is due to Ernest Solvay, a Belgian, and many of the devices still in use were patented by him. The process is based on the fact that when ammonium bicarbonate is added to a saturated solution of common salt, the ammonium salt dissolves and sodium bicarbonate separates as a solid; if filtered, dried, and calcined, it is changed to soda ash, or sodium carbonate, Na_2CO_3 :



This simple principle proved difficult of application, for ammonia is comparatively expensive, and unless it is all, or nearly all, recovered, the process cannot live.⁶ It was the nearly complete recovery of the ammonia which enabled Solvay to defeat the well-established Leblanc soda process.

In practice, a saturated salt solution is treated with ammonia gas, and this solution is then saturated with carbon dioxide; the resulting suspension of sodium bicarbonate in an ammonium chloride solution is filtered, and the sodium bicarbonate is dried and calcined. (See Fig. 19.) The ammonium chloride filtrate is treated with lime and steam to recover the ammonia. The danger of losing ammonia in this operation is not great; it is rather

⁵The Hönigsmann process produces about half the ammonia soda manufactured in Germany; the other half is Solvay soda.

⁶The minimum amount of ammonia in process is one-third the amount of soda ash it helps make; taking the low price of 5 cents for 1 lb. NH_3 , and 12 cents for soda ash, the ammonia in process is worth as much as the material produced.

in the gas leaving the carbonating vessels and in that leaving the calcining vessel that provision must be made to recover any ammonia which it may contain.

The carbon dioxide is obtained by burning limestone, and this furnishes at the same time the lime necessary for treating the ammonium chloride solution. It is clear that much fuel is required to burn the limestone, to calcine the sodium bicarbonate, and to raise steam for the ammonium chloride still. For the reaction proper, no fuel is required.



FIGURE 19.—Simplified diagrammatic flow sheet for the Solvay ammonia soda process. 1, brine tanks with ammonia absorption; 2, carbonating towers; 3, rotary suction filter; 4, calciner, giving the finished product; 5, milk of lime box for ammonia still below. The ammonia circulates. Lime kiln not shown.

The ammonia process has one imperfection, in that the chlorine which common salt furnishes is not recovered, except to a small extent; it passes to the sewer in the form of a solution of calcium chloride.

Ammoniating the Brine. As a rule, soda ash plants are located near the source of salt; thus the Syracuse, N. Y., plant formerly drew brines from the property, and now that a greater supply is needed, brine from Watkins Glen and the neighborhood is piped to Syracuse, about 20 miles away; the brines flow by gravity. At Wyandotte, Mich., huge deposits of salt are available. The great Dombasle plant in Lorraine, France, was also located there because of the almost limitless supply of salt in the region. Rock salt may be shipped in by rail, which, however, involves extra expense for freight, and rock salt is dearer than salt in brine (see table of production). The brine must be freed from calcium and magnesium salts, which tend to clog the carbonating towers in the later steps. This purification takes place in the same vessels in which the ammonia is absorbed. Such vessels are usually upright cylinders 15 feet high and 12 feet wide, with covers and conical bottoms. Ammonia dissolves in brine with evolution of heat, so that cooling cells hung from the cover and containing flowing cold water form

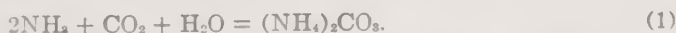
part of the absorber. Towers with shelves may also be used, with cooling coils outside.

The brine run into the absorber does not fill it, as space for expansion must be left, as the ammonia gas dissolves, the volume increases. At the same time, the solubility of the salt diminishes; by feeding in dry ammonia gas, thus avoiding moisture which would dilute the brine and disturb the conditions, the desired amount of ammonia may be introduced while the salt content remains at the saturation point for that particular ammonia content.⁷ A saturated salt solution at 15° C. contains 318 grams of NaCl per liter of solution, if no ammonia is present. A solution containing 60 grams of ammonia per liter is saturated with respect to salt if it contains 275 grams NaCl per liter, also at 15° C. This amount of ammonia requires only 206 grams of NaCl for the reaction, so that there is an excess of 69 grams of salt (33 per cent); because some ammonia remains as ammonium bicarbonate, since the reaction $\text{NH}_4\text{HCO}_3 + \text{NaCl} \rightleftharpoons \text{NaHCO}_3 + \text{NH}_4\text{Cl}$ does not run to completion (to 73 per cent for good operating conditions), the excess salt is really somewhat greater. The excess of salt is desirable, first because it drives the reaction to the right, and secondly, because it diminishes the solubility of the sodium bicarbonate.

A certain amount of carbon dioxide gas is sent into the absorber at the same time, but not enough to form ammonium carbonate; the calcium, most of the magnesium,⁸ and all the iron salts precipitate, and collect in the cone. After the proper amount of ammonia has been absorbed, the solution is settled and the clear ammonia-brine is blown by compressed carbon dioxide to the carbonating tower. A loss of ammonia during the treatment of the brine is avoided by connecting the outlet pipe of the absorber to a small tower with shelves, down which a fresh brine solution travels. By using a battery of absorbers, a supply of ammoniated brine is always ready.

There are two sources of carbon dioxide; one is the limestone kiln which furnishes gas containing 35 to 40 per cent CO_2 , the rest mainly nitrogen; the other source is the furnace in which the sodium bicarbonate is calcined; its gas may be as high as 95 per cent CO_2 . This second portion of the gas may be considered as circulating. In some plants, the two gases are combined in the pump house and no distinction is made; in others, they are used as indicated farther on.

Carbonating the Ammoniated Brine. In the Solvay system, carbonation is performed in towers with shelves, on the counter-current principle; the brine flows downward, the gas enters at the base and travels upward; the other systems are gradually adopting the towers. Two towers are used in many of the plants, instead of the original single tower; a short first tower, in which enough carbon dioxide is fed into the solution to form neutral ammonium carbonate:



⁷ Some salt may separate out as a solid, which then passes out with the settlings.

⁸ A magnesium salt content in the brine is not desired, and yet if the amount is small, and it escapes precipitation by the ammonia, which occurs because ammonium is a poor reagent for the purpose, its presence may be an advantage. Magnesia forms glass-like double salts with NaCl, which clog the walls of the apparatus, and prevent the carbonation of the soda by iron with its subsequent discolouration. The factory experience is that those plants which occasionally have their soda colored red consequently operate with magnesia-free brine.

In the second, taller tower, enough additional carbon dioxide enters to form the bicarbonate:



In other plants, the tower is a single unit, and there are several towers. If there are five, to take an example, four would be actively precipitating bicarbonate; the fifth one would receive the ammoniated brine from the saturators, as well as a moderate flow of lean gas (40 per cent CO_2) delivering at its bottom outlet a clear liquor, carbonated as required by reaction (1). The temperature is allowed to rise, reaching 32 to 40° C. [90 to 104° F.]. The partly carbonated ammoniated brine is an active solvent for incrustations of bicarbonate, which form in spite of the engineers' skill. This procedure then has as object (1), the partial carbonation of the ammoniated brine, (2), the removal of the crusts. Each tower in turn works four days, and on the fifth, it is rid of all obstructions. From the fifth tower, the clear liquor is divided and fed in equal amount to each one of the four working towers. The flow of brine through the fifth tower is four times faster than its flow through the working or precipitating tower.

On traveling down the working tower, the liquor meets a flow of strong

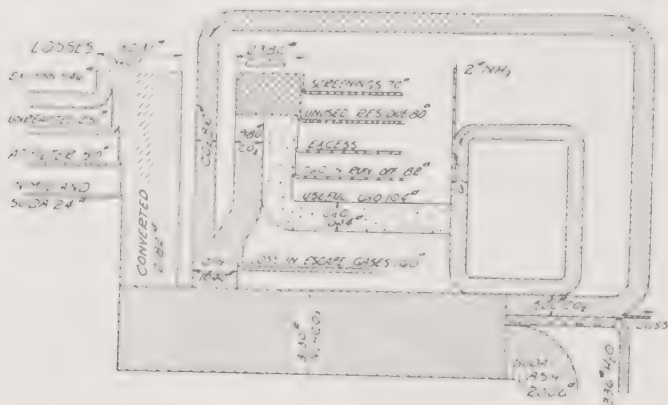


FIGURE 19a.—Diagrammatic sketch of the amounts of raw materials, circulated chemicals, products and discards in the Solvay process for soda ash. The widths of the columns and frames are in proportion to the weight of the materials they represent. (After Kirchner.)

carbon dioxide gas, traveling upward. Reaction (2) takes place, and simultaneously, reaction (3).



The temperature rises to 65° C. [149° F.]; by means of the cooling pipes provided in the lower sections of the tower (see Fig. 19a), the temperature may be lowered. It is essential not to lower it too far, however, for at low temperatures the sodium bicarbonate forms in such finely divided form that it cannot be filtered. The temperature of 26 to 27° C. [78.8 to 80.6° F.] has been found to be right for the production of grains of the proper size.

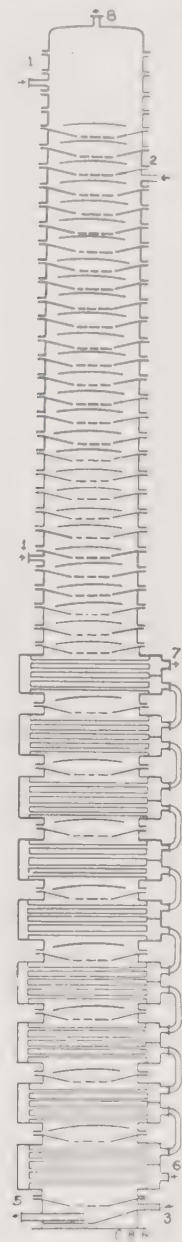
The tower consists of 28 upper sections, each 15 inches high, surmounting 9 lower sections which are 42 inches high. The material is cast iron. Each upper section has a floor with central opening, over which a dome-shaped

is supported by three brackets. The rising gas is deflected sideways by the domes. The lower sections have nests of cooling tubes; for the latter, wrought iron has proved a little more durable than cast iron. Other details

FIGURE 19b.—A carbonating tower in the ammonia soda process (Solvay); it is 69 feet high, and 6 feet in diameter.

1. Entry for ammoniated brine, used when the tower is being cleaned.
2. Entry for the ammoniated brine for the regular bicarbonate precipitation.
- 3 and 4. Carbon dioxide entries.
5. Outlet for the bicarbonate slurry.
6. Cooling water inlet, and
7. Its outlet.
8. Escape for uncondensed gases.

The supports for the domes not shown. (Modeled after Kirchner.)



may be obtained from Figure 19b. It may be well to point out that this tower is not a bubble tower; the rising gas has no liquid seals to overcome; it meets only the rain and foam of the descending liquid or slurry. Each shelf is flushed clean of deposit (within limits) by the descending liquid.

A tower such as shown has a daily capacity of 50 tons of finished soda.

The brine containing 60 grams of ammonia per liter requires 83 grams of carbon dioxide to form the neutral carbonate, a part of which is added in the absorbers. For the bicarbonate, an additional 83 grams must be added; in fact, a little more is required, for some carbon dioxide passes out unused from the top of the main tower. It carries away some ammonia, which is recovered with part of the carbon dioxide, in a supplementary tower fed with fresh brine.

The carbon dioxide gas enters at the base of the tower under a pressure of 30 pounds. As it rises, much of it is absorbed and the pressure drops. At the top of the tower the unabsorbed portion and the inert gas (nitrogen) pass through a supplementary tower where fresh brine removes any ammonia carried out.

The suspension is drawn off from the lowest compartment at frequent intervals, and fed to the trough of a continuous suction filter, of either the drum or the single-disk type. The cake is washed to remove all ammonium chloride; at the same time about 10 per cent of the bicarbonate is also dissolved and lost. In spite of the washing some ammonium bicarbonate is left in the cake, and its ammonia must be recovered; this is easily done, fortunately, for the ammonia passes out with the carbon dioxide on calcining the sodium bicarbonate, and the two gases together are sent to the carbonating tower.

Calcining Sodium Bicarbonate. A great variety of devices is used for calcining the bicarbonate, which is by no means an easy operation. In Europe a covered pan with semicircular cross-section and scrapers having a sidewise motion (Thelan pan), with outside firing, is much used. In America, the rotary furnace with horizontal axis, with outside firing, is favored; to prevent the forming of insulating crusts on the walls, some of the hot cake just discharged is mixed with the cake to be calcined. The gas is saved in all cases, and forced into the carbonating devices.



The discharged cake is light; for many uses, a denser cake is demanded; by calcining at a higher heat, the density is raised, but the dense soda ash of commerce is made by adding water to the light soda, and recalcining.

An analysis of a good commercial soda ash made by the ammonia soda process follows:

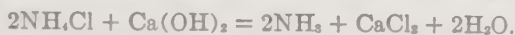
	Per Cent
Na_2CO_3	99.50
NaCl	0.20 to 0.25
Na_2SO_4	0.02
Insoluble	0.02
Moisture	balance

There is a tremendous sale for the bicarbonate to be used for baking powders, but for this purpose, the material must be purified, chiefly of ammonium salts. The crude sodium bicarbonate may be recrystallized, or a solution of soda ash may be carbonated. In 1939, 148,610 tons of refined bicarbonate were produced, and sold at \$26 a ton.

There is also a market for crystallized sodium carbonate, $\text{Na}_2\text{CO}_3 \cdot 10\text{H}_2\text{O}$, called sal soda, and made by cooling a solution of purified sodium

carbonate of the proper concentration. In 1939, 28,668 tons were produced, with a market price of \$25 a ton.

Ammonia Recovery. The bulk of the ammonia is present as ammonium chloride, NH_4Cl , in the filtrate from the bicarbonate; some ammonia is present as carbonate, carbamate, and bicarbonate. The recovery is performed in a modern ammonia still, such as the one shown in Chapter 14, in which the free ammonia (carbonate, sulfide) is driven off first, and then only is lime added to liberate the fixed ammonia (sulfate, chloride).



The calcium chloride passes out at the bottom of the still.

The run-off from still or tower contains no ammonia, or only a trace; it is blown by steam pressure to compartment settling tanks, and there settled; the clear liquor is removed, and the semi-solid lime mud carted to the dump.

The ammonium chloride liquor contains about one-third of the original salt (NaCl) unchanged; it is better to waste it than to have a less complete reaction. Part of the calcium chloride formed is wasted; but part of it is made into a concentrated calcium chloride liquor, the "brine" of the refrigerating plants; the diluted solution is also used to sprinkle on dirt roads.⁹ A considerable portion of the calcium chloride formed is evaporated to dryness, and used as stated below under Natural Calcium Chloride.

A lime kiln which allows the recovery of the carbon dioxide is used (Chapter 9). The gas from such a kiln contains the fire gases as well as the carbon dioxide from the limestone, and also dust. It is passed through a three-tray box, where it meets running water; the dust deposits, and the gas is cooled. From here it is forced into the carbonating tower.

Natural soda occurring mixed with sodium chloride and sulfate as well as magnesium salts may be isolated by treating the solution with carbon dioxide; sodium bicarbonate precipitates, is filtered off, and calcined to soda ash in horizontal rotary cylinders.¹⁰

The production in the United States for 1941* follows:

	Tons
Soda ash by ammonia process.....	3,512,000
Natural soda	120,000
Electrolytic soda	18,000

* *Chem. Met. Eng.*, Feb. 1942.

The selling price in 1939 was \$15.50 a ton for ammonia soda, and in 1929, it was \$19.00. The natural soda ash, valued at \$13.15 (1939), was produced from brines from Owens Lake and Searles Lake, in California.

The estimated distribution of soda ash sales is given in Table 7.

Natural Calcium Chloride. The mother liquor from salt crystallization contains mostly calcium chloride and magnesium chloride. A good part of such liquors is concentrated to a high salt content, and then "flaked" on a flaking or chip machine. The product is packed in paper-lined burlap bags and serves in the treatment of roads, coal and coke for dust prevention, on

⁹ Calcium chloride is hygroscopic and retains enough moisture to lay the dust.

¹⁰ The sesquicarbonate of sodium, often mentioned in the literature on natural soda, is $\text{Na}_2\text{CO}_3 \cdot \text{NaHCO}_3 \cdot 2\text{H}_2\text{O}$, and is also called "trona."

TABLE 7.—*Estimated Distribution of Soda Ash Consumed in the United States (in short tons).*[†]

Consuming industry	1939	1940	1941
Glass	744,000	810,000	970,000
Soap	215,000	225,000	260,000
Caustic and bicarbonate mfrs.	810,000	780,000	877,000
Other chemicals	620,000	710,000	785,000
Cleaners and modified sodas.	130,000	134,000	140,000
Pulp and paper	116,000	123,000	155,000
Water softeners	28,000	32,000	35,000
Petroleum refining	11,000	12,000	13,000
Textiles	43,000	45,000	68,000
Exports	80,000	58,000	87,000
Miscellaneous	164,000	200,000	250,000
	2,961,000	3,131,000	3,640,000

[†] *Chem. Met. Eng.*, February, 1941.

tennis courts, for refrigeration, and a variety of other purposes. In 1940 94,238 tons of this calcium-magnesium chloride valued at \$15.75 per ton were produced from natural brines in the United States.

A portion of by-product calcium chloride in the ammonia soda process is marketed in the form of flakes. In 1939, calcium chloride from all sources marketed as flakes amounted to 215,149 tons (77-80% CaCl_2), valued at \$18.90 a ton. Total calcium chloride production, which includes chloride both in the solid and in the liquid (solution) form, amounted to 239,354 tons in 1939.

SALT CAKE

Salt cake, the commercial anhydrous sodium sulfate, was produced originally by the action of sulfuric acid on salt (NaCl) in the pot and muffle process; within the last thirty years, the use of nitre cake instead of the free acid with the salt, and roasting the mixture in mechanical furnaces, has rendered the first process obsolete. It was partly to consume the nitre cake on the market that the mechanical salt-cake furnace was developed. It has been a success, but for a while there was a shortage of nitre cake; for example, in 1927, 153,615 tons were produced, but in 1935, only 27,933 tons were made. At the present time, the supply of nitre cake is again good, and will continue so during the war years, because of the large quantities of strong nitric acid required. When necessary, however, nitre cake may be made from salt and sulfuric acid in pots: $\text{NaCl} + \text{H}_2\text{SO}_4 = \text{HCl} + \text{NaHSO}_4$. This nitre cake, which has never seen nitre, may be mixed with salt and fed to the mechanical furnace just as well as true nitre cake. The amount of hydrochloric acid produced, let it be noted, is twice as great, and a market must be available for the additional amount. Less salt cake, with respect to the salt used and hydrochloric acid made, is produced when starting with sulfuric acid than when starting with nitre cake from the nitric acid still, for this nitre cake is already half salt cake.

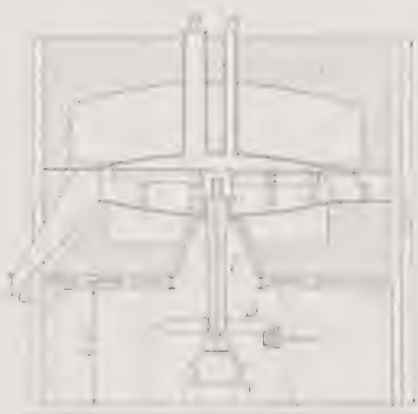
THE MANNHEIM MECHANICAL SALT-CAKE FURNACE

The best known mechanical furnace is the Mannheim.¹¹ It is an automatic device, with continuous operation; the labor is a minimum; and the labor of pulling out the fuming salt cake by hand rakes, a suffocating oper-

¹¹ German Patent 137,906 (1900), *Mechanischer Calcinirofen*, by the Mannheim Verein.

which is rendered unnecessary. When using nitre cake, the reaction is $\text{NaCl} + \text{N HSO}_4 = \text{HCl} + \text{Na}_2\text{SO}_4$; it takes place to near completion at $650^\circ \text{C. (1202}^\circ \text{F.)}$.

FIGURE 20.—Mannheim mechanical salt cake furnace, with hydrogen chloride as by-product. The charge enters at *A* and is discharged at *C*; the gas passes out at *B*. The eight plows are rotated from below, by gear *D*; the shaft may be water cooled at *E*.



The Mannheim furnace consists of a circular muffle of cast iron, 12 feet in diameter, with bottom and top dish-shaped; the inner height at the circumference is 20 inches, in the center 40 inches. A shaft penetrates it from below and carries four arms, each of which carries two cast-iron plows. The shaft is rotated slowly, 1 revolution in 2 minutes, by the gear and pinion indicated in Figure 20. The mixed salt and nitre cake is fed in from the top near the center, and is moved to the circumference by the plows. Plow 8 is wider than the others, and discharges the burned cake (now salt cake) through the opening of the chute (Fig. 21). Here the cake accumulates to some extent and is removed in small trucks to the storage bins. The discharged cake is yellow and turns white on cooling.

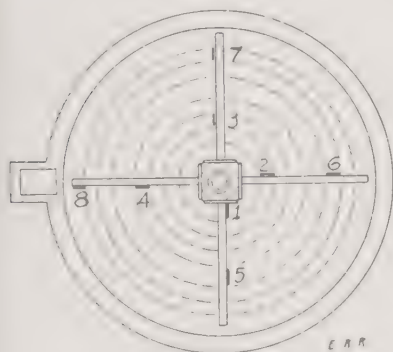


FIGURE 21.—Cross-section of the Mannheim furnace, showing bottom casting, the eight plows, and the lanes which they sweep.

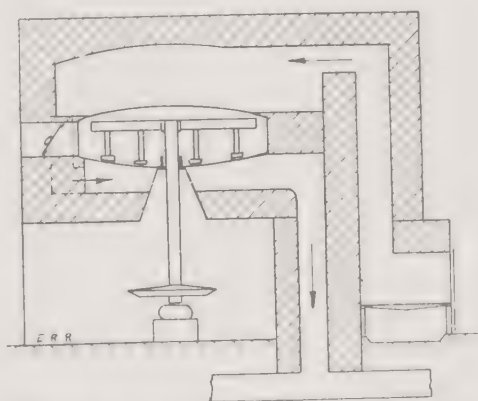


FIGURE 22.—Circulation of the fire gases around the Mannheim furnace.

Some of the details of construction of the muffle will be plain from the illustrations; the bottom and top are single castings. The sides consist of twelve curved castings which, when assembled, provide three doors; one

of these is over the discharge opening and chute. Each plow differs in length of shank; and each is slightly turned so that the cake is swept outward. The heat is furnished by a small fireplace. The fire gases enter over the muffle, heating the top; then travel to the under side by a passage in the brickwork and heat the lower side; from here they pass out to the chimney. (See Fig. 22.) The temperature is registered by a platinum-resistance pyrometer¹² placed in a protecting cast-iron tube reaching into the center of the muffle from above.

The salt used is rock salt, of the fineness of sand; it may be either purchased in that form, or if coarser, reduced in a swing hammer mill.¹³ The nitre cake, in pieces 1 foot across or smaller, is fed to a pot crusher¹³ or jaw crusher¹³; the product, the size of walnuts, is reduced to a coarse powder in a squirrel-cage disintegrator¹³ or a swing hammer mill. Salt and nitre cake are carefully mixed in some plants by placing equivalent quantities (250 pounds of salt and 700 pounds of nitre cake, for example) in a rotating cylinder and mixing for 15 minutes. In other plants merely dumping salt and nitre cake alternately into the hopper serving the screw conveyor which brings the cake to the feed pipe of the muffle is found to give sufficient mixing.

The reaction is preceded by a fusion; the nitre cake fuses first. The effect of high sulfuric acid on the fusion point of nitre cake is not so great as that of the moisture content; 10 per cent moisture lowers the fusion point from 320° F. (160° C.) for the dry cake with 37 per cent H_2SO_4 to 210° F. (99° C.); but 10 per cent sulfuric acid added to the dry nitre cake has almost no effect on its fusion point.

Temperature and Capacity. The temperature of the muffle is indicated by the pyrometer and is not kept constant, but is increased slightly as the wearing of the plows progresses; it lies between 625° and 675° C. The guide is the daily analysis of the salt cake. A well burned salt cake should contain 2 per cent or less NaCl , and 1.5 per cent or less H_2SO_4 ; if the cake runs higher in both impurities, the temperature may be increased. Other ways to control the quality are to change the relative proportions of salt and nitre cake, and the absolute weight fed in. In the 12-foot diameter muffle, six tons of good cake may be produced per day.

Length of Run. The plows need renewing every two months (approximate figure); the bottom casting may last two years, but one year is considered fair enough; the top casting and the sides will outlast several bottoms. The life of the plows may be lengthened by making the blades of Duriron¹⁴ and bolting them to cast-iron shanks.

Safety Flange. Should a plow become jammed against some foreign object a break may occur in the gears, which would be an expensive accident. This is prevented by fitting the pinion shaft with two flanges working through a pin whose size is just sufficient to carry the load. Any sudden resistance will break it, and at the same time indicate that the obstruction must be removed.

¹² Chapter 46.¹³ Chapter 44.¹⁴ Chapter 45.

Pot Stills. The nitre cake from the nitric acid retorts is supplemented, as already suggested, by the product obtained as still residue when salt is treated with sulfuric acid in the proportions indicated by the reaction $\text{NaCl} + \text{H}_2\text{SO}_4 = \text{NaHSO}_4 + \text{HCl}$.

The Laury Furnace. The second well known furnace installed in American plants is a two-stage rotary cylindrical furnace,^{14a} not unlike the cement furnace, but shorter and stouter.

The production of crude salt cake from all sources in the United States in 1937 was 241,347 tons valued at \$9.85 a ton, and in 1939, 226,151 tons valued at \$10.20 a ton. The low figure since 1925 was 98,727 tons in 1931, valued at \$15.45. In 1939 there were imported 148,794 tons; in 1940, only 73,027 tons. The decreased importations have stimulated the domestic industry (Bureau of the Census).

About 70 per cent of the crude salt cake produced and imported is consumed in the kraft pulp and paper industry. Salt cake forms part of the batch for window glass furnaces; it is the raw material for Glauber salt, sodium sulfide, and sodium thiosulfate. It serves in numerous minor rôles.

Refined anhydrous sodium sulfate produced domestically came to 42,489 tons, valued at \$16.20, in 1939 (Bureau of the Census).

Natural sodium sulfate sold or used by producers in 1939 totaled 137,479 tons valued at \$7.52 a ton; in 1940 the figure was 187,233 tons valued at \$8.20 a ton. The corresponding figure for 1935 was 38,706 tons, valued at \$9.75 a ton. The principal sources were Campe Verde, Yavapai Co., Arizona; Mina, Mineral Co., and Wabuska, Lyon Co., Nevada; Casper, Laramie Co., and Rawlins, Carbon Co., Wyoming. A new plant has been constructed at Dale Lake, California. In 1940, 9,518 tons of natural sodium sulfate were imported from Canada (Saskatchewan).

Synthetic Salt Cake. The stoppage of importations of salt cake from European countries, particularly from Germany, by the war has created a shortage so serious that a synthetic salt cake is manufactured. It consists of sulfur melted into soda ash, and is made as follows: The soda ash leaves the calciner and enters a screw conveyor; sulfur is added at that point. The hot ash melts the sulfur, and the action of the conveyor mixes the two, the sulfur coating the granules, producing a gray mass which has proved just as satisfactory in the kraft paper industry as true salt cake.¹⁵ It is being made at the rate of 400 tons a day (1941).

The Leblanc Process for Soda Ash. In the Leblanc process,¹⁶ salt is treated with sulfuric acid, giving sodium sulfate and hydrogen chloride; this first step was retained for the manufacture of hydrochloric acid with sodium sulfate as a by-product. The salt cake (sodium sulfate) mixed with limestone and coal is heated in a short rotary furnace, producing the "black ash," which, after leaching with water, gives a solution of sodium carbonate

^{14a} U. S. Patent 1,435,930 (1922) to N. A. Laury.

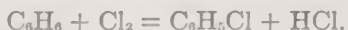
¹⁵ Read for example: "New ideas on use of salt cake in kraft pulp process," by Walter L. Savell, *Paper Mill and Wood Pulp News*, December 9, 1939.

¹⁶ Invented during the period of the French revolution, by Nicholas Leblanc, a physician. The inventor did not receive the promised prize from the government, and his plant suffered from the economic upheavals. For a century, civilization has enjoyed abundance of window glass and inexpensive soap, thanks to Leblanc's genius, but he himself died unrewarded, unthanked, in an asylum, by his own hand. See Hou, "Manufacture of Soda," 2nd ed., Chapter 1, New York, Reinhold Publishing Corp., 1942.

containing also caustic. This solution is evaporated by the waste heat of the black ash furnace, during which process it receives enough carbon dioxide to form all carbonate. The monohydrate $\text{Na}_2\text{CO}_3 \cdot \text{H}_2\text{O}$ separates, and is dehydrated completely in reverberatory furnaces. A part of the soda ash was made into caustic soda by treating the solution with lime, so that a lime kiln usually formed a part of the plant. The Leblanc process, even though no longer practiced, is one of the most famous processes in industrial chemistry. In the course of its development, fundamental engineering principles were recognized and firmly established (the counter-current principle, for example, in the Shanks system of lixiviation).

HYDROCHLORIC ACID

Hydrochloric acid is made (1) from salt, in salt-cake furnaces; (2) by burning electrolytically produced chlorine in excess hydrogen; (3) as by-product from the chlorination of hydrocarbons such as pentane and benzene



A fourth method¹⁷ employs chlorine and steam over heated coke (350° C., 662° F.) containing iron compounds as catalysts, or charcoal, to which iron oxide has been added.



Hydrogen chloride is a gas; on cooling to room temperature, it does not condense to a liquid, as does nitric acid, but must be dissolved in water. The ordinary commercial strength is 20° Bé., at 60° F. (15.5° C.), containing 32.46 per cent HCl. The system for absorption is essentially the same, whichever method for the production of hydrogen chloride is employed. As an example, the gas from a Mannheim furnace may be taken.

The gas from the Mannheim furnace passes through a 10-inch stoneware line, coated with tar to close the pores, to a short stone box, where it cools further and deposits most of the sulfuric acid which it carries. From the stone box, it passes to S-bend coolers or to Cellarius vessels set in running water; the cold gas then passes to the absorbing towers, where the solution in water or weak acid takes place. Tower No. 3 receives cold water, and delivers at the base a 12° Bé. acid, which is warm; before feeding it to No. 2, this acid passes through about 6 lengths of 1-inch glass tubing set in cold water. The cold acid is elevated to the top of No. 2 by a small automatic, hard-rubber-lined elevator, or by a "monte-jus",¹⁸ a gentle stream of air into a 1-inch glass pipe so that it forms gulleys of liquid which give a broken column easily pushed up. The acid solution from the base of No. 2 is cooled and fed to No. 1, where its maximum strength is obtained. The acid from No. 1, after cooling, is the 20° Bé. acid ready to ship. The daily production of a furnace furnishing 6 tons of salt cake is about 9000 pounds of 20° Bé. acid.

The towers are made of stoneware, usually in 10 sections, each 30 inches high, and 36 inches in diameter; the packing is coke, of carefully selected

¹⁷ German Patent 427,539 (1926); see also "Manufacture of hydrochloric acid from chlorine," Wilhelm Hirschkind, *Ind. Eng. Chem.*, 17, 1071 (1925).

¹⁸ Monte-jus is French for juice-raiser.

sies, or 3-inch spiral rings of stoneware. Three towers are sufficient for complete absorption, but in many plants four are used, and in the summer months, even five.

The gas is pulled through the absorbing system by a fan set at the exit from the third tower. (See Fig. 23.) The fan is protected from acid mist by a small coke box, so that a lead-lined fan or even an ordinary steel fan may be used. The suction exerted on the system is so regulated that it is felt at the muffle just enough to prevent the gas from passing around the working doors into the room. The strong gas may also be propelled by a stoneware fan set between the cooler and the first tower.

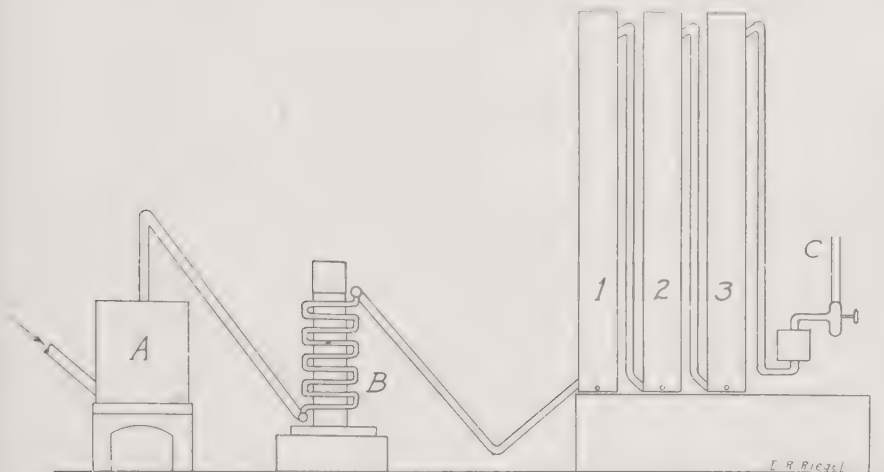


FIGURE 23.—Absorption system for hydrochloric acid; the gas enters dry box *A*, then cooler *B*, and the absorbing towers 1, 2, and 3; the exhausted gas passes out at *C*.

The stone box is built of sandstones which have been boiled in tar to prevent the acid from penetrating them; the stones are held together by cast-iron corner pieces and rods. The joints are made tight with rubber gaskets, or with asbestos cord smeared with china clay and linseed oil. The cooler may be made of S-bends, stoneware or fused quartz; for one furnace, there would be 5 rows of 4-inch S-bends, of which one is shown in the illustration; these pipes are cooled by a small amount of water trickling over them.

In some installations the towers are supplemented by Cellarius vessels of stoneware, about 46 inches long by 28 inches across, for acid cooling and adsorption (see Fig. 24). The design of this vessel provides for maximum absorption surface to a given total volume of solution. The function of the cooler S-bends may be performed by the Cellarius for gas cooling, of the same dimensions as just stated, but constructed in the opposite sense, so that it holds no liquid. The illustration (Fig. 24) will indicate the details.

Acid made by method (3) involves the removal of any unchlorinated hydrocarbon present in vapor form, then absorbing hydrogen chloride in water in a continuous system. For the recovery of hydrochloric acid obtained as by-product of pentane chlorination, a plant has been described.^{18a}

^{18a} "High-boiling solvents from natural gas pentanes," Lee H. Clark, *Ind. Eng. Chem.*, 22, 439 (1930), with 2 flow-sheets.

Acid made by method (2), namely by burning chlorine in hydrogen absorbed in towers with iron-free packing, is a water-white acid, essentially chemically pure. It more than meets the requirements for the chemist C. P. acid. A patented method¹⁹ avoids an excess of hydrogen with the consequent necessity of scrubbing the gas to be reworked, by using the undiluted gases in a system closed as to escape gases.

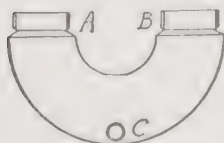


FIGURE 24.—Cellarius stoneware vessel for gas cooling; the gas enters at A and leaves at B; the vessel is set in running water, with only the bells protruding. C is the outlet for any liquid which may condense.

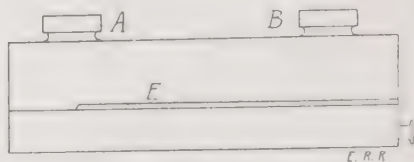
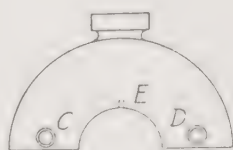


FIGURE 25.—Cellarius stoneware vessel for acid cooling and absorption; the gas enters at A and leaves at B; the acid solution enters at C and must travel to the rear of the vessel and then forward again in order to reach the outlet D, because dam E is in the way. The vessel is submerged in water.

Acid made by method (1) has a pale yellow color; it is shipped in glass carboys of 12-gallon capacity, set in a wooden protecting box, or in rubber lined wooden tanks, four tanks to a flat railroad car, or, to a lesser extent in steel tanks lined with wood impregnated with a wax tar. The content of arsenic is usually 0.0002 per cent As_2O_3 in the commercial acid; this low figure is due to the use of contact sulfuric acid which is made from carefully purified sulfur dioxide gas, itself obtained from selected ore or from sulfur. For certain purposes a still purer acid must be furnished; from the pot stills an acid is made with an arsenic content of 0.00005 per cent As_2O_3 . The production by all methods in 1939 was 78,848 tons on the 100% HCl basis valued at \$50 a ton, equivalent to 242,900 tons of 20° Bé. acid at \$16.23 a ton.

To illustrate the relative importance of the different processes, the following partial 1935 figures are given: hydrochloric acid 20° Bé. made from salt, 145,000 tons, from chlorine, 9950 tons, by-product and other, 14,000 tons. In 1939, 52,902 tons of hydrochloric acid on 100 per cent HCl basis (67%) were made from salt; while the acid made from chlorine, or obtained as by-product, gave a total of 25,946 tons (33%).

Hydrochloric acid is used to clean steel before galvanizing (dipping in melted zinc), in wire steel plants, in the manufacture of dyes, of phenol and for a number of minor purposes.

¹⁹ U. S. Patent 1,414,762; see also N. A. Laury, "Hydrochloric acid and sodium sulfate," New York Chemical Catalog Co., Inc., 1927, Chapter 8.

GLAUBER SALT

Glauber Salt ($\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$) is a purified salt cake; the Glauber plant is usually adjacent to the salt cake storage bin.

Salt cake is dissolved in hot water, best in a circular wooden tank with stirrer. Steam is passed in during the solution to make up for cooling to the air. The solution is made as strong as possible (32° B \acute{e} . hot), lime is added to neutralize the sulfuric acid invariably present, and to precipitate iron hydroxide and alumina. The liquor is allowed to settle, and the clear portion is run into the crystallizers. The muddy bottom is filter-pressed, and the filtrate sent to the crystallizers.

The latter are usually wooden forms lined with lead, 15 feet long, 6 feet wide, and 2 feet deep. On standing over night, crystals form; in the morning the mother liquor is run off by removing a wooden plug from the outlet in the bottom of the crystallizer, and the crystals are shoveled into low trucks on wheels; these are pushed to one of several openings in the floor, through which the crystals are dumped into the storage bin and shipping room below. The mother liquor is collected in a low tank and pumped into the dissolver, replacing, after being heated, a part of the water.

The crop of crystals in the winter months is greater than in the summer; in fact during hot spells it may happen that no crystals at all form. For this reason, a stock of crystals is accumulated in the winter and spring, and stored in bins closed on all sides. Ventilation must be avoided, for Glauber salt loses its water of crystallization on exposure to the air.

Glauber salt is crystallized from an acid liquor to obtain colorless crystals; from a neutral liquor, slightly colored brown crystals form. The composition is:

	Per Cent
$\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$	97.52
NaCl	21
Moisture	2.23
$\text{Fe}_2(\text{SO}_4)_3$01
CaSO_4022
Free acid008

In a few plants, iron crystallizers are used, and the liquor is kept alkaline; this results in a product slightly off color.

Glauber salt is used extensively in the textile industry; in 1939, 34,493 tons of Glauber salt were produced; the market price was \$15.65 a ton. Its manufacture is interesting not only because of the high purity obtained but because, by making the first hot solution strong enough, no concentration of any kind is needed. This principle is followed in the chemical industries whenever possible.

SODIUM SILICATE

Sodium silicate is made by fusing together sand and soda ash in the proportions of 100 pounds of sand to 52 pounds of soda ash. Its formula is somewhat indefinite; it lies between $\text{Na}_2\text{O} \cdot 3\text{SiO}_2$ and $\text{Na}_2\text{O} \cdot 4\text{SiO}_2$. It occurs chiefly as a thick syrup, a water solution of the solid (30° to 40° B \acute{e} .). Sodium silicate is commonly called water glass, because when solid it is a glass, and because this glass, unlike lime-soda glass (ordinary window glass)

is soluble in water. The melting is performed in large tank furnaces similar to the window-glass furnace.²⁰ The materials are introduced in batch at intervals; the product may be drawn off continuously or periodically. A mixture of sodium sulfate and coal may be used instead of part of the soda ash.

As the melt leaves the furnace, a stream of cold water shatters it into fragments; these are dissolved by means of superheated steam in tall, narrow steel cylinders with false bottoms,²¹ and the resulting liquor clarified.²² Sodium silicates are sold in solutions which vary from the most viscous, 69° Bé., to thinner ones, reaching finally 22° Bé. solutions, adapted for paints. The dry material in the form of a powder is also on the market and is made by forcing the thick liquor through a very fine opening into a chamber swept by a rapid current of cold air, which carries off the moisture.²³ Because sodium silicate is hygroscopic, powdered sodium sulfate is sometimes incorporated with the solid silicate²⁴ to prevent caking. In composition, the sodium silicates may be varied from $1 \text{ Na}_2\text{O} \cdot 2\frac{2}{3} \text{ SiO}_2$, to $1 \text{ Na}_2\text{O} \cdot 3.9 \text{ SiO}_2$; they differ in alkalinity from pH 13.2 for $\text{Na}_2\text{O} \cdot 2\frac{2}{3} \text{ SiO}_2$ to pH 10.8 for the $\text{Na}_2\text{O} \cdot 3.9 \text{ SiO}_2$ silicate, measured in 1 per cent solution. In the concentrated solutions, the pH is not very different. Each of the commercial ratios results in a liquid with special properties, rendering it the proper selection for a specific purpose.^{24a}

The uses of sodium silicate are surprisingly numerous; it is added in the crutching of soap²⁵; it serves to impregnate wood, to weight silk, as mordant, as a heat-resistant binding agent, to clarify juices and solutions, to render bricks and cements non-porous, as a detergent, and as an adhesive particularly in making corrugated paper boxes.

BROMINE AND BROMIDES

When the brines from which table and dairy salt is made contain bromides, the bromine may be recovered from the mother liquors. The oldest process, still in use, is to concentrate the mother liquor and to treat it in a stone still (untarred) with sulfuric acid and sodium chlorate (formerly with manganese dioxide); a current of steam carries off the bromine liberated. An earthenware coil receives the mixed steam and bromine and condenses both, by water cooling; two layers collect in the stoneware receiver; the lower one is the dark red, liquid bromine; the upper one, bromine water. They are separated, and the bromine, from the water layer may be recovered by blowing with air or natural gas. This lean bromine gas is treated separately; it is passed through a small stoneware tower filled with moist iron filings, and a strong solution of ferric bromide forms, from which the bromine is displaced by chlorine gas. Bromine is a liquid which boils at 63° C. (145° F.)

In another process the brine is treated directly with chlorine gas; still

²⁰ Chapter 11.

²¹ U. S. Patent 1,138,595.

²² U. S. Patent 1,132,640.

²³ German Patent 249,222.

²⁴ U. S. Patent 1,139,741.

^{24a} Several interesting and instructive bulletins on this subject may be obtained by addressing the "Philadelphia Quartz Company, Philadelphia, Pa." See also "Sodium metasilicate as an industrial alkali," James C. Vail, *Trans. Am. Inst. Chem. Eng.*, 25, 123 (1930).

²⁵ Chapter 32.

coldest process is based on the fact that on electrolyzing a bromide bearing brine, the bromine is liberated first, the chlorine only later.

Crude bromine is purified from chloroform, its chief impurity, by a redistillation, passing the vapor over iron filings which retain the chlorine.²⁶

Bromides are made by saturating caustic soda (or sodium bromide, NaBr) with bromine; a smaller amount of sodium bromate is simultaneously formed, $6\text{NaOH} + 3\text{Br}_2 = 5\text{NaBr} + \text{NaBrO}_3 + 3\text{H}_2\text{O}$. Bromides are valuable pharmaceuticals; bromine serves in the manufacture of certain dyes²⁷ as a disinfectant; its irritating and suffocating properties have led to its use as a war gas.²⁸

At Wilmington, N. C., bromine is obtained from sea water,^{28a} which contains 0.0064 per cent (average) of bromine; 1800 gallons of sea water must be treated for each pound of bromine obtained. This plant is now the largest American producer. A second plant using sea water as source is the Freeport, Texas plant of the Dow Chemical Company, also a large producer. Bromine is obtained also at Midland and Saginaw, Michigan, in Ohio, and in West Virginia. A large part of the world's supply formerly came from Stassfurt, Germany. A salt deposit rich in bromides and readily flooded by controlled amounts of sea water occurs in Tunis.²⁹

Bromine and bromine compounds sold or used by producers in the United States during 1940 came to 59,266,275 pounds with the average value of 9.85 cents a pound. The production figure is three times that for 1936.

The use of ethylene bromide with tetraethyl lead as an antiknock compound³⁰ in gasoline engines has meant a large consumption, supplied first by imports, but more and more, by domestic producers. The increasing production of bromine has made this possible. In 1930, 3,024,484 pounds of ethylene bromide were imported; in 1935, only 477,005 pounds had to be imported.

OTHER PATENTS

U. S. Patent 1,165,815 (1916) to Thelen and Wolf, on a mechanically operated salt-cake furnace; German Patent 325,314, on preheating the charge for the Mannheim furnace; German Patent 295,073, to Henry Howard, of Massachusetts, on serving salt and sulfamic acid direct to Mannheim furnace. U. S. Patent 1,907,987, soda ash; 1,940,459, manufacturing soda ash; 2,035,441, apparatus for manufacture of sodium carbonate monohydrate; 2,038,025, sodium sesquicarbonate from bicarbonate; 1,928,540, manufacture of sodium bicarbonate; 1,921,505, low apparent density sodium carbonate; 1,868,949, sodium sulfate production; English Patent 375,039, electric heat for the salt-sulfuric acid reaction; Can. Patent 396,040; U. S. Patent 2,242,507, to make sodium sulfate and ammonium chloride; 2,208,175, production of sodium sulfate. German Patent 489,917 and 516,348, mechanical salt cake furnace; U. S. Patent 1,853,330, distillation and concentration of hydrochloric acid; German Patent 558,553, same, with the aid of added CaCl_2 ; German Patent 535,355, same, and recovery of acetic acid and HCl from the same vapors; 1,902,801, continuous process of preparing liquid bromine; 1,917,762, extracting bromine from dilute solutions; 1,930,143, bromine recovery from spent developers; 1,919,721, preparation of bromates; Brit. Patent 523,607 (1940), on bromine from sea water; Russ. Patent 54,404 (1939); U. S. Patent 2,245,514, and 2,251,353, all three concerning bromine.

²⁶ A list of patents relating to these various processes will be found on page 93, *Dept. Interior Bull.* No. 146; see reading references; the first two patents were U. S. Patents No. 460,370 (1891) and No. 1,232 (reissue 1892).

²⁷ Thus eosine, Chapter 28.

²⁸ Chapter 34.

^{28a} "Commercial extraction of bromine from sea-water," Leroy C. Stewart, *Ind. Eng. Chem.*, 26, 361-369 (1934), with 20 illustrations.

²⁹ "The future demand for bromine," C. R. De Long, *Ind. Eng. Chem.*, 18, 425 (1926).

³⁰ Chapter 24.

PROBLEMS

1. (a) A plant intends to manufacture 300 tons of Solvay ammonia soda per day the soda to be 98.8 per cent Na_2CO_3 . How much salt will be required per day, if it NaCl content is 99 per cent, for the actual conversion? How much salt is required since the carbonating towers consume 66 per cent of the salt, the rest being wasted? At what point or points is the salt lost which is not used? (b) What is the weight of the bicarbonate of soda made as intermediate product?

2. The ammonia NH_3 which takes part in the reaction is about one-third the weight of the soda ash produced. For the production of the soda ash specified in Problem 1, how much carbon dioxide is needed for the actual final product, and how much limestone, 95 per cent CaCO_3 , must be calcined in order to obtain it? Is the lime obtained simultaneously sufficient for the regeneration of the fixed ammonia, or is it an excess, or is there a deficiency? (Leave fire gases in kiln out of consideration.)

3. Referring to Problems 1 and 2, let there be once again the amount of ammonia in process as found to have reacted, mainly in the absorbers, and some in the tower liquor and filtrate from the bicarbonate. How much would the ammonia be worth (at 5 cents a pound NH_3), compared to the value of the soda ash produced? The amount of carbon dioxide in process is again as much as leaves the plant in the soda ash, mainly returned from the calciner. How much calcium chloride in solution form leaves the ammonia still, in its run-off?

4. A plant manufactures soda of 99.5 per cent purity. The amount of salt actually transformed in the operation is 37 tons. The reaction $\text{NH}_4\text{HCO}_3 + \text{NaCl} = \text{NaHCO}_3 + \text{NH}_4\text{Cl}$ takes place to the extent of 75 per cent. How much salt is taken originally, how much left unused; what is the tonnage of soda ash made, if the calcination is performed without loss? What is the weight of bicarbonate of sodium, expressed as dry NaHCO_3 ?

5. In a Mannheim furnace, there are charged per day 6500 pounds of salt mixed with a certain amount of nitre cake. If the nitre cake has the theoretical composition for NaHSO_4 , how many pounds of the latter must be charged per hour? Assuming the recovery of salt cake to be 98 per cent, how many tons of salt cake will be collected per day?

6. From the ash charged as described in Problem 5, hydrochloric acid is recovered with an efficiency of 89 per cent; it is made into 31 per cent HCl (about 20° Bé.) How many pounds of acid will be collected per day?

7. 4100 pounds of 96.5 per cent salt cake is made into Glauber salt, which has the analysis shown in the text. How many pounds of Glauber salt will be obtained, assuming that the mother liquors are worked up constantly so that the yield is 94 per cent? What will be the factor, salt cake to Glauber salt? (1 lb. salt cake produces x lbs. Glauber salt.)

8. It is desired to prepare 9 tons of sodium silicate syrupy, to test 38.8° Bé. The composition of the dissolved silicate is to correspond to $\text{Na}_2\text{O} \cdot 3.36\text{SiO}_2$. The specific gravity given corresponds to 36 per cent of the 3.36 silicate. How much soda ash 99 per cent, and how much sand 100 per cent will be required, the yield being assumed to be 92 per cent?

9. A brine is saturated and contains on analysis NaCl 298 grams per liter; CaSO_4 5.1 g.p.l.; CaCl_2 .81 g.p.l.; CaCO_3 15 g.p.l.; MgCl_2 .48 g.p.l. The non- NaCl materials restrict the amount of NaCl which the equal brine would hold at saturation. If that amount of salt is proportional to the equivalent of the foreign salts, what is the amount of NaCl which the brine will hold at saturation?

10. The crude Solvay NaHCO_3 crystals always contain ammonium in the ratio of 5NH_3 to 95 Na , and it cannot be washed out; it is assumed that a double salt forms. It is only on calcining that the ammonia is liberated. NaCl and Na_2SO_4 on the other hand wash out readily at the filter. For the weight of bicarbonate in Problem 1 (b), and in Problem 4, how much ammonia does that represent per day? In what way is it saved to the system?

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"The culture of certain silicate gardens." James G. Vail, *Ind. Eng. Chem.*, 26, 113 (1934).

"Glauber salt in North Dakota." Irvin Lavine, Herman Feinstein and Earl Skene, *Chem. Met. Eng.*, 42, 681 (1935).

"Die Sodafabrikation nach dem Solvay-Verfahren." Julius Kirchner, Leipzig, S. Hirzel, 1930.

Wherever possible, the salts of sodium are used in preference to those of other metals, for the salts of sodium are soluble and cheap. The cheapness is due to the abundance of common salt, NaCl , the source (as to metals) of nearly all other sodium salts.

Chapter 4

Sodium Sulfide, Sodium Thiosulfate (Hypo), Anhydrous Bisulfite of Sodium, Sodium Hyposulfite

In a modern chemical establishment manufacturing a number of heavy chemicals for the general trade, there is a relation between the various sections, in that the product of one becomes the raw material for the next. Sulfuric acid, the first product, is the only exception; it is made entirely from purchased materials (sulfur or pyrite), or from by-product sulfur dioxide gas from a smelter. The preparation of nitric acid from sulfuric acid and sodium nitrate in retorts is accompanied by the production of nitre cake and this must be supplemented, when necessary, by its manufacture from salt and acid in the pot stills; the nitre cake fused with salt gives hydrochloric acid and salt cake (Na_2SO_4). A large amount of salt cake is sold as such; the remainder is heated with coal or coke and made into sodium sulfide, Na_2S . By-products of this are sodium carbonate, Na_2CO_3 , and sodium sulfite, Na_2SO_3 , which are properly worked up into sodium thiosulfate, $\text{Na}_2\text{S}_2\text{O}_3$, usually called "hypo" from its old name of hyposulfite, now abandoned. Not all sodium sulfide is made from salt cake, for although the latter is the cheapest raw material, furnaces, leaching tanks, and other equipment are required; for small-scale operations, soda ash and sulfur are more suitable. In large plants, such as the one described above, caustic soda, chlorine, and soda ash are not usually included, but all those products which require sulfuric acid for their manufacture¹ are part of the plant. Soda ash is usually purchased in considerable quantities, for it serves to make anhydrous bisulfite of soda, NaHSO_3 , sodium hyposulfite (hydrosulfite), $\text{Na}_2\text{S}_2\text{O}_4$, and, following the older process, sodium thiosulfate, $\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$; plants for these three products properly belong to an establishment which includes the manufacture of sulfuric acid, because the sulfur dioxide required may be taken from the burner house by simply erecting a pipe line. To complete the description, a power house for steam and electric current generation would be included; also water pumps for cooling, washing, and absorbing water; shipping facilities, and offices.

A modification of the set-up outlined will make good the lack of nitre cake, and sodium sulfate from nitre cake, by purchasing natural sodium sulfate. The nitric acid would then also have to be purchased from synthetic ammonia plants, or the ammonia might be purchased, and the oxidation performed in the old nitric plant, remodeled for the purpose.

¹ Chapter 2; but not superphosphate (Chapter 7), which is a specialty.

SODIUM SULFIDE

Sodium sulfide, Na_2S , has become extremely important as a depilatory,² in the manufacture of sulfur dyes, and, in solution, as a solvent for the same sulfur dyes.³ It was formerly produced altogether in the form of crystals, $\text{Na}_2\text{S} \cdot 9\text{H}_2\text{O}$, which in the commercial form contained about 30 per cent Na_2S ; the crystals are brown, whereas pure sodium sulfide crystals are colorless. These crystals are still made, but the greater part of the sulfide is now marketed in the form of concentrated sodium sulfide with 60 per cent Na_2S , as solid cakes and lumps, or as flakes ("chips"). The method may be outlined as follows: Salt cake (or roast cake) from the Mannheim furnace mixed with coal is heated in a reverberatory furnace; a melt is produced which is raked out and either dissolved in water at once, or allowed to cool to solid cakes which are later leached with hot water. The solution is made strong enough so that when it is cooled in shallow pans, crystals of $\text{Na}_2\text{S} \cdot 9\text{H}_2\text{O}$ form. To produce the 60 per cent sulfide, the crystals are melted in special pots and water driven off from the hot liquid; on cooling, a black solid with red fracture forms. Another way consists of boiling down the first solution after filtering or settling, until the sodium sulfide content is a little above 60 per cent.

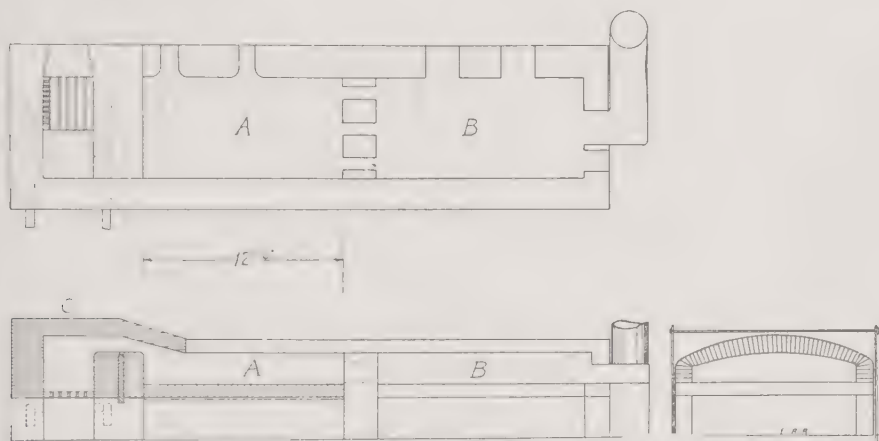


FIGURE 26.—Sodium sulfide furnace, reverberatory type; A, reduction hearth; B, preheating chamber. The fireplace and half of the bridge wall are of hard firebricks; C, the hearth of alunite or aluminate bricks.

Reverberatory Furnace. A reverberatory furnace is shown in Figure 26; it is a low arch furnace with a fireplace separated from the hearth by a bridge wall. The fire gases strike the roof over the fireplace and are deflected onto the charge on the hearth; the low arch forces intimate contact between fire gases and charge. From the furnace proper the gases pass to the preheating chamber, of dimensions similar to those of the hearth, and from there to the stack. For a furnace whose hearth is 12 feet long and 8 feet wide, the charge is 1000 pounds of salt cake⁴ and 500 pounds of coal screen-

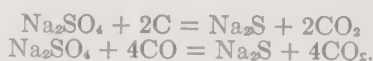
² Chapter 36.

³ Chapter 28.

⁴ Instead of salt cake, nitre cake was formerly used; the escaping sulfuric acid caused a cloud at the top of the stack, which caused much difficulty with municipalities. It was thought that by substituting salt cake the cloud would vanish; but to everybody's surprise, it continued. In this case, it is due to sulfurous sodium salts; these may be removed from the stack gases by a Cottrell precipitator; see Chapter 43.

ings. Such a charge is shoveled into the rear of preheating chamber, where it is warmed by the outgoing gases for an hour. It is then pushed with hoe to the working hearth and heated there, with occasional stirring, for another hour, when it is ready to be pulled out. Instead of shoveling in the charge, it may be fed in from an overhead bin through an opening in the arch. Melted sulfide is extremely corrosive, so that the construction of the furnace is a special one. The floor of the hearth consists of alunite or other basic bricks, set upright on their smallest face. These bricks rest on several thicknesses of asbestos paper soaked in silicate of soda solution; such an underlining has been found efficient in preventing the escape of melt. The alunite bricks are placed in a solution of silicate of soda for some hours just before laying. The hearth side of the bridge wall is also lined with alunite bricks, while the fireplace side and the arch over the whole furnace are of ordinary fire bricks. The rear wall is usually lined with a hard firebrick. Such a furnace will last 8 to 12 months, when it must be rebuilt.

In order to insure a high yield the atmosphere in the furnace must be reducing one; the fire gases should contain one or several per cent carbon monoxide and no oxygen. Such fire gases are obtained by building a deep bed of coal on a fireplace of rather small dimensions, using soft coal and forced draft. The reactions on the hearth are:



There are several ways in which the melt may be handled on leaving the furnace. A simple and efficient way is to pull the charge into 8 or 10 buggies on wheels, each holding 80 to 100 pounds, so that one man can handle them. Another way is to pull the charge into two steel boxes on low trucks. In either case the melt is allowed to cool; during the cooling of the cakes some further reduction takes place. The cold cake is broken with a sledge and fed to an edge runner⁵ washed by a constant flow of warm water. A solution of sodium sulfide with suspended matter results, which is elevated to a settling tank. In the older plants, the cake is fed to a jaw crusher on the floor, then elevated to one of four leaching tanks which are worked in series; each tank accommodates one day's melt. The fresh melt is wetted with the wash from the melt of the day before, and this wash in turn has first rested on the nearly spent melt of two days before; the fourth tank is being emptied. In this way each melt is leached three times.

A totally different way is to pull the melt into a ladle and to bring it over a dissolving tank with a stirrer. The fluid melt, still hot, is run into the water, which is thereby heated; this operation is extremely noisy. It utilizes a part of the heat of the melt, however, and saves labor, so that it will probably become standard, at least for large plants. The suspension may be settled or filter-pressed using iron wire filter cloth; the press cake is made up with water once more, filter-pressed again, and the filtrate used in the dissolving tank.

The melt in the cakes is 60 to 65 per cent Na_2S ; such rich melts flow less easily than melts contaminated with unreduced sulfate or with carbonate.

⁵ Chapter 44.

The sulfide liquor obtained by any of these variations is hot, and of such strength that after it is run into shallow iron pans, crystals deposit over night. The mother liquor contains sulfide, and also sulfate, sulfite, and carbonate; it may be concentrated, when all the salts other than sulfide precipitate, leaving a concentrated solution of sulfide which may usually be crystallized; in some cases it may contain so much silicate that it will not crystallize. The precipitated salts are dissolved in water and the solution used for making thiosulfate. The brown crystals with 30 per cent Na_2S may be sold as such, or they may be placed in iron pots over a fire, melted, and enough water removed to raise the content of Na_2S to 60 per cent. The liquor may be run into concentrating pans directly and evaporated to the higher strength; the difficulty in that case is that the sulfate, carbonate, and similar impurities deposit during the concentration and coat the bottom of the concentrating pans, causing them to become locally overheated, which results in leaks.

The 60 per cent liquor may be run into shallow flat pans, where it solidifies over night; it is then broken and shipped as lumps. There are many other ways to fix the final shape of the product; the best one is to feed a thin layer to a water-cooled rotating drum, actuated by means of a ratchet; a knife detaches the cake, and the thin strips fall and break into still smaller flakes, called chip sulfide.⁶ In this form, solution at the consumer's plant is greatly facilitated. The color of chip sulfide is red; like any other form of sulfide it must be stored in air-tight, thin, steel drums; otherwise it turns green because of the formation of sulfate and carbonate.

New Types of Sulfide Furnaces. The old reverberatory furnace is still the most reliable way to manufacture sulfide, although many proposals for new types of furnace have been made. The aim of the newer furnaces is to reduce labor to a minimum by a continuous operation, largely automatic. On one of these furnaces, a rotary style⁷ is proposed with carbon monoxide gas, prepared in auxiliary vessels, as reducing agent and fuel. Several German proposals are promising also; one⁸ involves the use of a Bessemer pear such as is used for making steel, and still another⁹ proposes ovens with pendulum or shaking motion. Two blast furnaces have been patented; one proposal¹⁰ allows the melt to solidify; in the other¹¹ the fluid melt is either tapped at intervals or drawn off continuously. In the latter furnace, as well as in one proposed by H. K. Moore,¹² the fluid melt is dropped at once into a "quench tank." Finally, studies in the application of the electric furnace to the manufacture of sodium sulfide have been made¹³ and were applied commercially in Italy during the war of 1914-18.

The United States production in 1939 was 31,481 tons of 60 to 62 per cent Na_2S , valued at \$54 a ton.

⁶ U. S. Patent 915,633.

⁷ U. S. Patent 1,397,497.

⁸ German Patent 388,545.

⁹ German Patent 389,238.

¹⁰ German Patent 255,029.

¹¹ German Patent 273,878.

¹² U. S. Patent 1,130,317.

¹³ *Chem. Abstracts*, 15, 3423 (1921).

SODIUM THIOSULFATE

Sodium thiosulfate ¹⁴, $\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$ or "hypo," is the agent employed in photography for dissolving the unreduced silver salts, and in textile mill as an "antichlor." It is made in two ways; the first one is independent of any other process, and requires soda ash and brimstone; the second make use of by-product sulfide liquors and is dependent upon a sulfide plant; its sulfur dioxide may be drawn from the burner house of the sulfuric acid plant generally forming part of a large establishment. It is customary in the second kind of plant to have in reserve soda ash and brimstone, so that in case the by-product liquor fails, these materials may be used instead. The same apparatus serves without any change, and burner gas is the source of sulfur dioxide, as before.

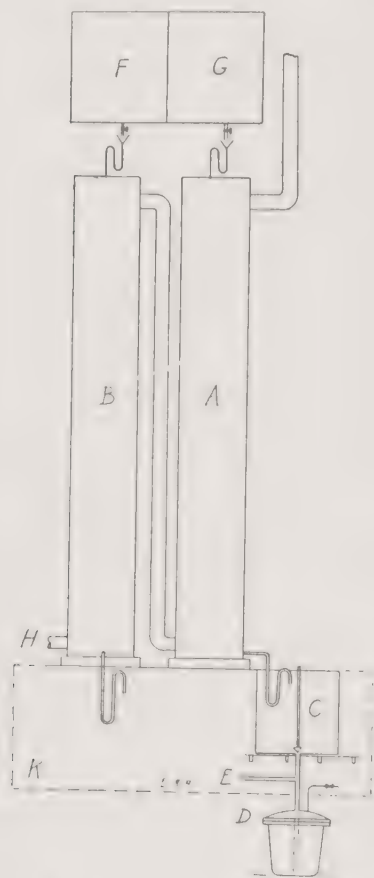


FIGURE 27.—A simple plant showing the working principles for making sodium bisulfite solution. Soda ash solution in tank *G* is fed to the first lead tower, *A*, where it meets the weak gas from the top of the second lead tower, *B*. The liquor from *A* collects in *C*, is run into the lead-lined cast-iron pot *D*, used as a blowcase, and forced through *E* to tank *F*, from which it is fed to tower *B*, meeting fresh gas entering at *H*. The finished liquor collects in the storage tank *K*.

The Soda Ash-Brimstone Process. Soda ash is dissolved in hot water and the solution (26° Bé.) pumped to a small storage tank at the top of the first of two absorption towers. These are of lead supported on wooden beams, and are filled with hardwood sticks, except in the lower part where a small chamber of hard acid bricks is provided. The nearly spent sulfur gas from the second tower (second with respect to the liquor) enters at the base and meets the descending soda ash solution which absorbs all the remaining sulfur dioxide. The partly gassed liquor from the first tower is elevated to

¹⁴ An old name for the same substance is sodium hyposulfite, from which the name "hypo" originated.

the top of the second tower wherein it meets the sulfur dioxide gas fresh from the burners; the soda ash is completely changed to sodium bisulfite, which runs out through a seal at the base of the tower and is collected in lead-lined receiving tanks.

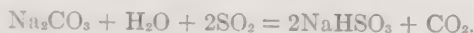
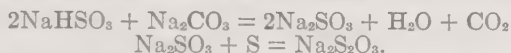


Figure 27 indicates the dimensions and disposition of the apparatus. The nitrogen, oxygen, and carbon dioxide pass out of the first tower to a small stack.

Sulfur dioxide may be made by burning brimstone in iron pans cooled from below by air, and set in brick work; or, a special patent burner may be installed, such as the Glens Falls, (N. Y.) rotary burner, the Chemico spray burner (Chapter 1), the Vesuvius burner with shelves, and others.

Formerly the bisulfite liquor, with 22 per cent SO_2 content, was an important product; it has been replaced by anhydrous bisulfite of soda, a powder with 60 per cent SO_2 , described later. By means of soda ash, the bisulfite liquor is changed into neutral sulfite, and this is heated with powdered brimstone¹⁵ in a brick-lined, cast-iron vessel with a stirrer. A solution of sodium thiosulfate results; it is concentrated hot in a boiler from 36° Bé. to 51° Bé. After settling, this liquor is run into lead-lined or steel crystallizers and allowed to cool. When iron crystallizers are used, a crust of the crystals is left on the sides and bottom to avoid contamination.



After two or more days, the mother liquor is run off, the crystals $\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$ are shoveled to centrifugals which remove adhering mother liquor, washed by a short spraying from a hose, and dumped to a conveyor leading to the interior of a cylindrical steel wire screen. The screen consists of two sizes, a six-mesh half which receives the unassorted crystals, and a three-mesh screen which forms the rear half.¹⁶ The fines drop through the six-mesh wire as the screen slowly rotates; the pea size drops through the three-mesh wire, while the coarser pieces, the "crystal" size, roll off at the far end of the wire. No drying of the crystals is necessary.

A fine crystal product of uniform size called "granulated hypo" is made by cooling the 51° Bé. liquor in circular steel pans 10 feet in diameter and 3 feet deep, in which a two-armed scraper slowly revolves while the liquor cools.

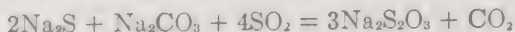
Sodium thiosulfate crystals effloresce so readily in air that they must be packed at once in air-tight containers, cartons or paper-lined barrels.

The By-Product Sulfide Liquor Process. The carbonate and sulfite which separate from the sulfide liquor while it is in process of concentration are made up with water; the adhering sulfide is also dissolved. This liquor becomes the raw material for sodium thiosulfate manufacture. In the plants which filter the suspension from the "quench tanks," and make up the first mud with water again, then filter once more, this second filtrate becomes the raw material for hypo; the first filtrate is essentially sulfide.

¹⁵ The crushing of brimstone is not without danger.

¹⁶ Compare Chapter 44.

The most satisfactory relation of the carbonate and sulfide (the sulfide is usually very low) is about 8 per cent Na_2S and 6 per cent Na_2CO_3 , where the reaction



takes place during the gassing period. An excess of sulfide over this amount must be avoided, as it may lead to a loss of useful materials in the generation of H_2S :



Some of this hydrogen sulfide will be changed into sulfur by sulfur dioxide, but it is manifestly cheaper to supply sulfur in the form of brimstone, if any is needed. Technical sodium sulfide always contains some polysulfides, and these supply some sulfur which reacts with such sulfite as may be present in the original liquor. Should the carbonate run high and the sulfur low, brimstone may be added to change the sulfite formed (the bisulfite is avoided¹⁷) into thiosulfate.

The sulfide-carbonate liquor may be treated with sulfur dioxide gas, the regular burner gas with 7 per cent SO_2 , in towers. Instead of a single passage of the liquor through a rather tall tower, many passages through a shorter tower may be substituted; these are then called circulating towers. The liquor is run into a large tank and pumped at a rapid rate to the top of the tower, which has wooden shelves. As the liquor cascades from shelf to shelf, fresh surfaces are exposed and the absorbing liquid exhausts the gas readily. The gassed liquor at the base of the tower runs back into the original tank. The tower may be 20 feet high, 4 feet in diameter, of steel lined with bricks; the wooden shelves are perhaps 10 inches apart. Each shelf covers only about two-thirds of a circle, and the openings are staggered, so that the liquor changes direction constantly. Two or more towers may be used, the gas passing from one to the other to insure its exhaustion.

After sufficient gassing, the liquor is filter-pressed through cotton duck cloth and concentrated in a steel boiler with a steam chest.¹⁸ The crystallization and further steps are the same as described under the soda-ash brimstone process. It will be noted that in normal running the sulfide by-product liquor requires no brimstone addition.

In 1939, there were produced 25,714 tons of sodium thiosulfate, $\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$, valued at \$44.50 a ton.

ANHYDROUS BISULFITE OF SODIUM

The commercial methods¹⁹ for manufacturing anhydrous bisulfite of sodium, NaHSO_3 , a cream-colored crystalline powder, differ in detail, but are alike in general principle, namely, in passing 7 or 8 per cent sulfur dioxide into a suspension of soda ash in the mother liquor saturated with sodium bisulfite²⁰ from previous batches. When a new plant is started, a suspension of soda ash in a saturated soda ash solution may be used. There is produced a suspension of anhydrous bisulfite, which is passed

¹⁷ Acidity due to NaHSO_3 is detected and measured by a titration with caustic in presence of phenolphthalein; Na_2SO_3 is neutral to phenolphthalein, but alkaline to methyl orange; it is measured with any carbonate present, by a titration with standard acid, in the presence of methyl orange; NaHSO_3 is neutral to methyl orange.

¹⁸ Chapter 43.

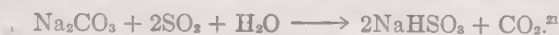
¹⁹ U. S. Patents 1,099,177; 1,084,436; 1,023,179.

²⁰ As soon as soda ash is added to the mother liquor, its sodium bisulfite is changed to sodium sulfite, and the suspension is soda ash in sodium sulfite solution.

through centrifugals. The wet powder remains; the mother liquor is collected in the "emulsion" tank and treated with soda ash to produce the suspension which is sent through the process again. The wet powder is dropped to a conveyor leading to a circular shelf drier with six shelves, rotating arms move the material from shelf to shelf, dropping it through alternate circumferential and central openings. The shelves are hollow steel, with steam circulation. The powder issues from the bottom warm and dry; a small inclined bucket conveyor lifts it into a hopper from which barrels are filled by pulling a slide.

By using a building with several stories, the material may be moved by gravity, except for feeding the soda ash to the emulsion tank, and lifting the soda ash emulsion to the absorbers. These operate in two stages; the first-stage absorbers, on the top floor, receive the soda ash emulsion and the sulfur dioxide gas which has already passed through the second-stage absorbers. The latter, on the floor below, receive the suspension from the first-stage absorbers by gravity, and the fresh sulfur dioxide gas from the sulfur or pyrite burners. Here the soda ash is completely transformed to anhydrous bisulfite, and this suspension is fed to the centrifugals on the floor below; the drier is on the ground floor, on a level with a railroad car floor.

The function of the drier is merely to remove adhering moisture; the anhydrous bisulfite is produced as such in the suspension.



The neutral sulfite, Na_2SO_3 , is made, for example, by the action of soda ash on the sodium bisulfite; it is sold both in the anhydrous form and as crystals, $\text{Na}_2\text{SO}_3 \cdot 7\text{H}_2\text{O}$. The production in 1939 was 11,213 tons of the two kinds together, with an average value of \$62 a ton.

The absorbers are steel tanks lined with bricks, 15 feet high and 15 feet in diameter; the tight-fitting, closed top is cast-iron covered with lead. A 4-bladed hard lead propeller, working through a stuffing box, makes 100 revolutions per minute; the gas inlet pipe reaches about 1 foot below the liquid. A 10-inch main brings the gas, and 3-inch lines (3 to each tank) deliver it into the suspension. The spent gas from the first-stage absorber is pulled out by a fan and discharged into the air. The propeller shaft is lead-covered, as is also the rod carrying the plug valve which closes the discharge hole in the bottom.

Anhydrous bisulfite of sodium is used in the manufacture of dyes, and in their application to fiber; as an "antichlor"; in the sterilization of casks for beer and similar beverages, and for several other purposes.

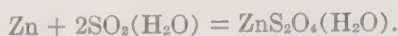
SODIUM HYPOSULFITE (HYDROSULFITE)

Sodium hyposulfite, $\text{Na}_2\text{S}_2\text{O}_4$, called hydrosulfite in the trade, is a convenient form of the powerful reducer which is used for the reduction of

² In Patent 1,023,179, the reaction is given as: $2\text{NaHSO}_3 + 2\text{NaCO}_3 + 2\text{H}_2\text{O} + 4\text{SO}_2 = 6\text{NaHSO}_3 + 2\text{CO}_2$. The product is therefore held to be solid bisulfite of sodium, NaHSO_3 , which is known to exist. In many processes, however, it is more likely that the anhydride, $\text{Na}_2\text{S}_2\text{O}_5$, forms, for several samples from different manufacturers contained 61.9, 64.1, 63.5, 62.8 per cent SO_2 respectively. Sodium bisulfite contains only 61.5 per cent SO_2 and as a contamination of sulfate is always present, and sulfate at times it is probable that in some cases the product is anhydride, whose content of sulfur dioxide SO_2 is 67.3 per cent.

certain dyes; before its advent in the trade, it had to be prepared at the textile mills and used at once. Formerly, it had to be imported, chiefly from Germany; it is now manufactured in the United States.

The method²² includes four steps. (1) Powdered zinc of 93 per cent purity is suspended in water in a lead container provided with cooling coil and a stirrer. Pure sulfur dioxide, best from a tank of liquid sulfur dioxide, now an article of commerce,²³ is led in, fast at first, and more slowly near saturation. The temperature is kept below 30° C. The color changes to black, to gray, finally to cream.



(2) The content of the saturator is transferred to a lead-lined steel tank with stirrer; a soda ash solution is added, in slight excess over the amount indicated by the reaction



Zinc carbonate precipitates, while sodium hyposulfite remains in solution. The suspension is filtered on a stationary suction filter²⁴; the cake is washed several times, but only the first wash is added to the filtrate; the subsequent ones are pumped into the saturator.

(3) The filtrate reaches the salting-out tank; its strength is adjusted to 15 per cent $\text{Na}_2\text{S}_2\text{O}_4$, and to this liquor salt (NaCl) is added, 300 gram for each liter of solution. The hydrated sodium hyposulfite, $\text{Na}_2\text{S}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$, separates in the form of needles. The suspension is heated rapidly to 60° C. and kept there until all the crystals have been transformed to the anhydrous sodium hyposulfite, $\text{Na}_2\text{S}_2\text{O}_4$, a sand-like, crystalline powder.²⁵ The crystals are allowed to settle, the supernatant liquor is run off, and hot denatured alcohol is added. (4) The crystals suspended in the alcohol are transferred to a steam-jacketed vacuum pan, the alcohol sucked off after settling, and three portions of alcohol run in so that no water might remain. By warming and causing a vacuum, the adhering alcohol is removed (and recovered), leaving in the pan the dry, sandy material, of light gray color, 90 per cent pure.

The 1939 production of sodium hyposulfite, $\text{Na}_2\text{S}_2\text{O}_4$, amounted to 14,732,083 pounds, valued at 15.2 cents a pound.

OTHER PATENTS

U. S. Patent 1,946,089, on anhydrous (85 per cent) sodium sulfide, granular, free running, and with rapid solution in cold water; 2,018,359, depilatory agent; 2,024,624, depilatory method and apparatus.

PROBLEMS

1. A sulfide furnace receives a charge of 1000 pounds of salt cake per hour; theoretically, 549.5 pounds of Na_2S should be recovered, but the recovery is only 77 per cent. The product is made into chip containing exactly 62 per cent Na_2S . How many pounds of chip are produced per day? The salt cake is never pure; the calculation must be based on a content of 95 per cent Na_2SO_4 .

2. Sodium thiosulfate crystals $\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$ of 97 per cent purity are produced by the reaction $2\text{Na}_2\text{S} + \text{Na}_2\text{CO}_3 + 4\text{SO}_2 = 3\text{Na}_2\text{S}_2\text{O}_3 + \text{CO}_2$, from by-product liquors

²² "Sodium hydrosulfide as a dry powder," L. A. Pratt, *Chem. Met. Eng.*, 31, 11 (1924).

²³ Chapter 19.

²⁴ Chapter 42.

²⁵ The transition point of the hydrated salt to the anhydrous form is 52° C.

from the sodium sulfate process; the production of hypo crystals is 20,000 pounds per day. Assuming that the reaction takes place to the extent of 96 per cent, how many pounds of Na_2S , Na_2CO_3 and SO_2 will be required?

READING REFERENCES

"The manufacture of sodium thiosulfate," L. Hargreaves and A. C. Dunningham *J. Soc. Chem. Ind.*, 42, 147T (1923).

"Die Verfahren der anorganische chemische Industrie," zweites Berichtsjahr, Dr. W. Stiegel, Berlin and Vienna, Urban und Schwarzenberg, 1935.

The patent and other literature as indicated in the text.

The manufacture of caustic soda directly from salt in solution, in single operation, has passed, in the last forty years, from an exciting possibility to the humdrum of everyday technology. Caustic soda is a cheap soluble alkali; lime is still cheaper, but is almost insoluble. Caustic soda is a strong alkali. Soda ash and ammonia are mild ones.

Chapter 5

Caustic Soda and Chlorine

Caustic soda, NaOH, a white solid, extremely soluble in water, is made by causticizing soda ash by lime and by the electrolysis of salt, NaCl, in water solution, with the simultaneous production of chlorine and hydrogen. In the offing is a third method, namely, by the addition of metallic sodium to a concentrated caustic solution, with certain precautions.

The production figures (U. S.) for the two main processes are:

	1939*	1940†	1941†
Caustic soda by lime-soda process.....	523,907	505,000	573,000 tons
Electrolytic caustic	426,250	595,000	677,000

* Bureau of the Census.

† *Chem. Met. Eng.*, 49 (1942).

1940 was the first year in which electrolytic caustic passed lime-soda caustic.

CAUSTIC SODA BY CAUSTICIZING

Soda ash in the form of a 20 per cent solution is treated with milk of lime in slight excess, in a tank fitted with an agitator. The solution is warm (85° C.; 185° F.). After an hour, the agitator is stopped and the precipitated calcium carbonate settles; the strong (12 per cent NaOH) caustic liquor is decanted. Wash water is run into the agitator, and after some time is allowed to settle out its mud; the clear liquor is run off to the weak liquor tank. The mud is washed once more, yielding the "wash" which is run to the wash water tank. The mud is discharged from the tank; it may be carted to the dump, or it may be filtered and calcined, yielding a lime suitable for further causticizing. The first and second liquors are evaporated to 50 per cent NaOH concentration in single- or multiple-effect evaporators, and if solid caustic is desired, to the final strength of 98 per cent or better in cast-iron pots over a free flame. In many plants, the 12 per cent NaOH liquor is used directly.

It has been found that choosing the concentrations of the reacting liquors as stated gives a good conversion (98 per cent) in the reaction $\text{Na}_2\text{CO}_3 + \text{Ca}(\text{OH})_2 \rightleftharpoons 2\text{NaOH} + \text{CaCO}_3$, and yet does not impose too high a fuel cost for evaporation. The lime is slaked with just enough of the wash water to form the hydrate, and then with only as much more as is required to make the milk; so prepared, the rate of settling of the calcium carbonate is 1.5 feet per hour instead of 0.28, when making the milk at once. Using a rotary slaker, the rate of settling becomes 7.81 feet per hour.¹ To utilize

¹ W. E. Piper, *Am. Inst. Chem. Eng.*, 24, 1 (1930).

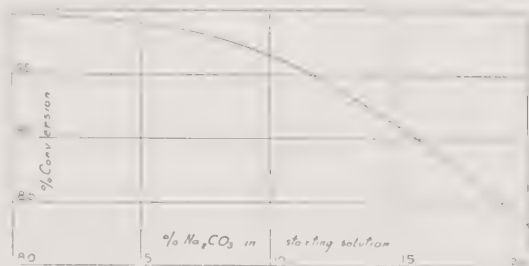
all the wash water, solid soda ash and the solid slaked lime may be fed into it.

Instead of batch operation, which the description just given presents, continuous operation may be secured, with classifiers for purifying the milk of lime, and thickeners to hasten the separation of mud from clear liquor. The two best-known systems are the Dorr and the Mount. In the study of the evaporation of the caustic liquor to high strengths, the use of diphenyl vapors around a nickel tube was found promising.²

An analysis of caustic soda made by causticizing soda ash manufactured by the ammonia soda process shows a low chloride content, an important consideration in many uses. The composition is:

	Per Cent
NaOH	98.62
NaCl	0.30
Na ₂ CO ₃	0.90
Na ₂ SO ₄	0.18

FIGURE 28.—The conversion of soda ash to caustic by lime, for various concentrations of the soda ash in the starting liquor. The lime added is Ca(OH)₂ with no additional water. Example: Starting with a 10% Na₂CO₃ solution, 96.5% of the sodium carbonate will be converted.



CAUSTIC SODA BY ELECTROLYSIS

In tonnage, electrolytic caustic soda is less than that made by causticizing; it represents, however, a totally different method of working, namely, the application of electric current to chemical decompositions and regroupings.

Many cells have been devised in which the decomposition may be performed; they may be listed under three heads: the diaphragm cells, the mercury cells, without diaphragm, and the bell-jar type, without diaphragm and without mercury. The first diaphragm cell was the Townsend cell, which is represented in modified forms by the Allen-Moore, Nelson, Vorce, Hooker, Marsh, and other cells. The original mercury cell was the Castner, also an American invention, still in use in the United States; modifications of it, giving good service, are the Whiting and the Solvay. An important representative of the bell-jar type is the Billiter cell.

For all cells it is customary to purify the salt solution and to use it as strong as possible, that is, not far from saturated, about 25 per cent NaCl. The manufacture of diaphragm cells, in a few words, involves the preparation and purification of the saturated salt solution; electrolysis of this solution in the cell, wherein half the salt is transformed into caustic; concentration of this mixed solution with separation of the salt as the concentration rises; and final evaporation to anhydrous caustic over an open

² W. L. Badger, C. C. Monrad and H. W. Diamond, *Am. Inst. Chem. Eng.*, 24, 56 (1930).

fire. For the mercury cells, the procedure is about the same, but the caustic liquor issuing from the cell is free from salt. This is an important advantage if the liquor is to be used on the spot; it requires no concentration, for a salt content need not be removed. The liquor issuing from the diaphragm cell, with as much salt as caustic, could not be used as such for most purposes. For the manufacture of solid caustic, this advantage disappears. The diaphragm cells produce a final caustic with 2 per cent NaCl; this small amount is not objectionable for the important applications of caustic. The great purity in this respect of caustic from mercury cells (0.2 per cent NaCl) does not bring it a premium. The general procedure for the bell-jar type process is similar to that for the diaphragm cells.

The decomposition efficiency of cells varies between 50 and 60 per cent; a high figure is the more important the dearer the electrical energy purchased. Decomposition efficiency is the ratio of the salt decomposed to the total salt; thus if 6 parts of salt are decomposed into caustic, and 4 parts of salt remain unchanged in the liquor (both determined by titration), the decomposition efficiency is 60 per cent. The decomposition voltage for commercial cells lies between 3.5 and 5, with 4.5 perhaps an average. The theoretical decomposition voltage for NaCl in water solution is 2.25.³ The voltage efficiency is the theoretical decomposition voltage divided by the actual decomposition voltage, here $2.25 \div 4.5 \times 100 = 50\%$. The actual voltage applied will vary with the current density, that is, the number of amperes per square unit of surface of electrode; the higher the current density, the higher the voltage necessary. A part of the difference in energy represented by the voltage figures appears as heat; the temperature of the diaphragm cell, for instance, maintains itself at about 60° C. In general, the rough estimate is made that the potential drop for each cell is 5 volts.

The current efficiency, or better, the cathodic current efficiency, varies from 90 to 96 per cent in the best-designed cells, under even running; it may drop to 75 per cent or even less, for a variety of causes. The cathodic current efficiency is the weight of caustic formed divided by the theoretical weight of caustic which the amount of current per hour (ampere hour independent of voltage) should have formed (1.491 grams), multiplied by 100.⁴

The energy efficiency is the product of the voltage efficiency and the current efficiency, here $0.96 \times 0.50 \times 100 = 48\%$.

The amount of current required to liberate a gram-equivalent at each pole is the faraday, which is equal to 96,580 coulombs (1 coulomb = 1 ampere-second). One ampere-hour equals 3600 coulombs, so that the amount of material liberated by 1 ampere-hour is:

$$\text{Chlorine } \frac{3600}{96.580} \times 35.46 = 1.3218 \text{ grams}$$

$$\text{Caustic } \frac{3600}{96.580} \times 40.01 = 1.4913 \text{ grams}$$

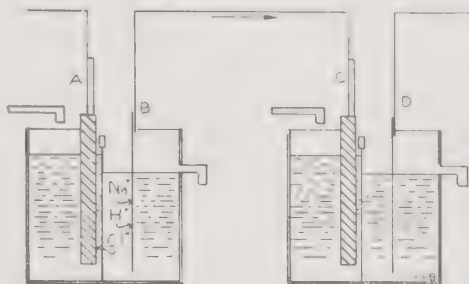
³This value is based on the Gibbs-Helmholtz equation, and takes into account the heats of formation of the substances represented in the equation $\text{NaCl} + \text{H}_2\text{O} = \text{NaOH} + \frac{1}{2}\text{Cl}_2 + \frac{1}{2}\text{H}_2$.

⁴Compare "The fundamentals of electrolytic diaphragm cells," by H. K. Moore, *Am. Inst. Chem. Eng.*, 13, I, 42 (1920).

THE ELECTROLYTIC CELL

The two cells in Figure 29 show the essential parts of an electrolytic cell. The current, which is always direct current, is said to enter at the anode and to leave at the cathode.* In a brine, there are present sodium ions Na^+ and chloride ions, Cl^- besides the ions resulting from the hydrolysis of water, the hydrogen ion, H^+ , and the hydroxyl ion, OH^- . The chloride ions give up their negative charge (one electron) at the anode, and become yellow chlorine gas, Cl_2 . The sodium ions receive a negative charge at the cathode and become metallic sodium; this dissolves as such in the mercury (or lead) of the mercury type cell. In the case of the diaphragm cell, a secondary reaction takes place, the sodium decomposing water to form sodium hydroxide and hydrogen gas: $2\text{Na} + 2\text{H}_2\text{O} = 2\text{NaOH} + \text{H}_2$. In the Whit-

FIGURE 29.—Cells for the electrolysis of solutions of sodium chloride in water. The chloride ion, Cl^- , forms chlorine gas at the anodes, marked A and C; the sodium cation, Na^+ , forms sodium at the cathodes, and the hydrogen ion, H^+ , forms hydrogen gas at the cathodes; the latter are marked B and D. A diaphragm divides the anode brine compartment from the cathode compartment.



ing mercury cell, the amalgam first formed is made to react with water in a separate chamber, to form also caustic and hydrogen. The several cells are so connected that the current passes from the cathode of one cell to the anode of the next; the path of the current then lies through the metallic bar to the anode, through the liquid to the cathode, through a metallic connection to the next anode, and so on to the last cathode, which is connected to the terminal at the generator. In passing through the metal, the current causes no change; in passing through the brine, a decomposition of the salt into chlorine and sodium takes place. In the Townsend cell, caustic gradually accumulates near the cathode; to prevent its free diffusion toward the anode, a wall may be placed in the cell, forming two compartments. Diffusion of caustic to the anode would result in the formation of sodium hypochlorite, thus reducing the yield. This wall allows slow passage of the solution and free passage of the sodium ions; by maintaining the level in the anode chamber higher than in the cathode chamber, the hydrostatic flow of liquor is toward the cathode, nullifying the tendency of the NaOH to diffuse toward the anode. The permeable wall is usually asbestos paper or cloth suitably coated, and is called the diaphragm.

Another explanation for the formation of hydrogen gas in the diaphragm cell—preferred by many scientists—is that the hydrogen ions are discharged directly at the cathode, acquiring an electron, and forming the hydrogen molecule. The reaction which expresses this view might be written: $\text{Na}^+ + \text{Cl}^- + \text{H}^+ + \text{OH}^- = \text{Na} + \frac{1}{2}\text{Cl}_2 + \frac{1}{2}\text{H}_2 + \text{OH}^-$. It will be noted

*It would be more correct to say that electrons enter at the cathode, and leave at the anode, but the general custom should be observed.

that enough water is assumed to be ionized to furnish hydrogen and hydroxyl ions. The main support for this view is that the single potential for hydrogen is lower than that for sodium. As fast as the hydrogen ions deposit, new ones form by ionization of water molecules.^{5a}

PURIFICATION OF THE SALT SOLUTION

The salt may be in the form of a natural brine, an artificial brine, or rock salt. The purification of the latter includes such steps as may be required for the brines. The salt is shoveled from the box car into an underground hopper feeding an inclined belt elevator or bucket elevator by means of which it is raised to the dissolving tank. This is kept filled, and warm water is pumped in at the base and allowed to overflow at the top; during its passage through the salt it becomes saturated. Instead of a wooden tank, a concrete tower (short) may be used. The brine is collected in the treating tank, where sodium carbonate and bicarbonate are added in amount just sufficient to precipitate the calcium and magnesium salts. After settling to remove the coarse suspended particles, the cloudy liquor is decanted periodically into a series of large, wooden settling tanks which act at the same time as storage. The tanks are in series, and the brine overflows very slowly from one to the next, so that they function as catch basins. The solution passing from the last basin is almost clear. It is filter-pressed, but the content of solid is so low that the press need be opened but once a week. Instead of filter-pressing, the brine may be filtered through a sand bed. The filtered salt solution, containing about 25 per cent NaCl, is elevated to a tank above the cells and fed through a constant-level boot to a 3-inch pipe with side branch for each cell. The method of regulating the amount fed to the cell varies considerably; one of the simpler schemes is to insert a horizontal plate with small orifice in the vertical branch leading to the anode compartment, with a glass sleeve immediately below the orifice plate to permit observation of flow. The size of the orifice determines the rate of flow.

THE DIAPHRAGM CELLS

All diaphragm cells embody the principle of enclosing the anode compartment by a diaphragm, as originally proposed by C. P. Townsend; therefore, they are all referred to as Townsend cells. However, the modified constructions of the later cells have been of the greatest importance; furthermore, they differ from each other radically. It is chiefly for convenience that they are grouped together under the same name. Of these modified Townsend cells, a sub-group would be formed by the Townsends-Baekeland⁶ and Hooker cells, which are evidently related. Both have liquor in the cathode compartment, the kerosene in the Townsend-Baekeland cell being replaced by caustic liquor, with a residual salt content, in the Hooker cell. It seems certain that no cell remains in commercial operation with kerosene in the cathode compartment, so that the Hooker cell may be taken

^{5a} The deposition potential for H^+ from a solution with pH 7 is about 0.414 volt; even with a hydrogen overvoltage on iron of 0.8 v., the total is only 1.213 v. The single potential for sodium is 2.7146 v. in a normal solution of sodium ions, somewhat less in the 4.3 normal solution here. The hydrogen ions therefore deposit first.

⁶ "The new electrolytic alkali works at Niagara Falls," Leo Baekeland, *Electrochemical and Metallurgical Industries*, 5, 269 (1907). Also 7, 313 (1909), by the same author.

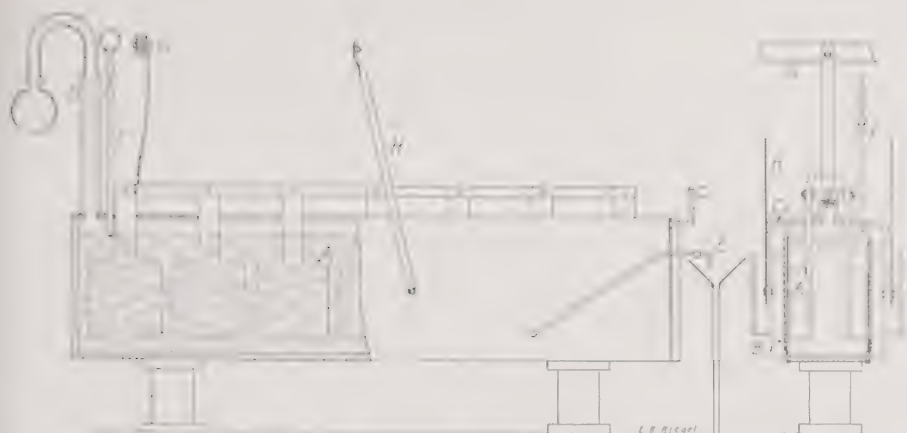
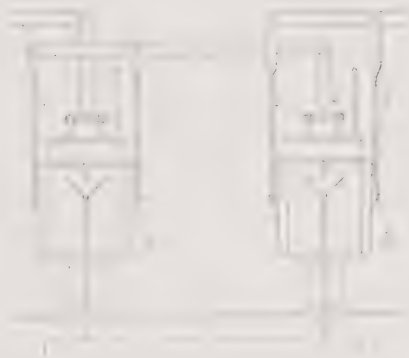


FIGURE 30.—Side view and vertical cross-section through Townsend cell. *A*, graphite anodes; *B*, perforated cathode with diaphragm; *C*, outlet for hydrogen; *D*, chlorine outlet; *E*, discharge for caustic liquor; *F*, brine feed; *G*, current entering anode; *H*, current leaving cathode. The level of the caustic liquor in the cathode compartment is lower than the level in the anode compartment.

as typical of the diaphragm cells which have liquor in the cathode compartment.

The Hooker "E" Cell. The Hooker "E" cell avoids the reworking of the chlorine-laden anode liquor, necessary in the Backeland cell, by dispensing with kerosene, allowing instead the partly causticized liquor to accumulate in the cathode compartment. The brine is fed to the anode compartment, but no liquor is drawn from it; instead, liquor is drawn from the cathode compartment. The rate of feed to the anode compartment and the withdrawal from the cathode compartment are equal. The level in the anode compartment is higher than in the cathode chamber. The flow of liquor toward the cathode is strong enough to prevent diffusion of the caustic to the anode.

FIGURE 31.—End view of two Townsend cells showing the electrical connections; 1, cathodes in cell *A* connected to 2, anodes in cell *B*; 3, cathodes in cell *B* connected to anodes in cell *C*, not shown.



The Hooker "E" cell, like the Townsend-Backeland, is a rectangular narrow box, as indicated in Figures 30 and 31. The 4500-ampere unit would be about 14 feet long, 3 feet high, and 18 inches in thickness. Each 14 by 3 feet side piece is of cast iron, forming a narrow vertical chamber just behind

the perforated cathode carrying the untreated asbestos paper diaphragm. The base and the two narrow sides are of reinforced concrete. Each cell has for anodes two rows of 9 graphite slabs, each row facing one of the diaphragms carried by the cathode plate at a distance of 1 centimeter. In 60 such cells are united in a bank of cells, a current of 4000 to 4500 amperes would be sent through them (passing from the cathode of one to the anode of the next; see Figure 31) at 300 volts, each cell requiring a little less than 5 volts. To indicate the capacity of such a bank, its output may be estimated at 10 tons of caustic per day, or about 330 pounds per cell (98 per cent NaOH).⁷ Two or four such banks of cells are placed together in one cell house. The Hooker cell works with high current densities,⁸ 100 amperes per square foot of cathode surface; its cathodic current efficiency is 96 to 97 per cent. The temperature of the cell liquor is 60° C. (140° F.).

The Hooker "S" Type Cell. The most advanced type of diaphragm cell is the "S" cell, with square cross-section^{9a}; it consists of a concrete top piece, a concrete bottom (set on short legs), and a central steel frame which



FIGURE 32.—Arrangement of graphite anode blocks and cathode fingers in "S" cell; much simplified.

carries the multimembered cathode. The cell is proportioned to have minimum (outer) surface-to-volume ratio, in order to diminish the radiation loss. It is heavily lagged, also to conserve heat. The cell is closely packed with cathode and anode branches, with only a 4-inch central free passage, for anolyte circulation. The cathode is of the finger type, the fingers reaching in from the sides; they are made up of crimped steel wire covered with asbestos, forming a diaphragm.^{9b} The anode is made up of graphite slabs, set in a bitumen-covered lead base plate, which receives the current; the slabs reach up from below between the fingers of the cathode, so that every vertical face of the cathode is close to a similar graphite surface. A single broad-faced connection at the cathode of one cell carries the current a short distance to the single post feeding the anode of the next cell. The cell operates at a higher temperature than its predecessors, at 85° C. (185° F.), which permits the use of a lower voltage; the heat need not come from converted electrical energy; it is merely saved, and transferred from the outgoing products to the incoming brine, both by means of double-walled pipe

⁷ "Description and views of the Townsend cells and the Niagara Falls plant of the Hooker Electrochemical Company," A. H. Hooker, *Trans. Am. Inst. Chem. Eng.*, 13, 1, 55-60 (1920).

⁸ The current density means the current in amperes per unit surface. An increase in current density requires an increase in voltage.

⁹ The higher the temperature, the less the resistance; higher than 90° C. is avoided because of the greater action of the products on the cell walls; 60 to 70° C. is the general range.

^{9a} U. S. Patent 1,866,065, with six sketches.

^{9b} U. S. Patents 1,862,244, 1,865,152.

cells lead in the cell wall, and by interchangers outside of it.⁹ In the Hooker "S" cell of 7000 ampere size, the anodic current density is 0.068 ampere per square centimeter (0.445 amp./sq. in.), the cathodic current density is 0.058 ampere per square centimeter (0.378 amp./sq. in., equivalent to 54 amp./sq. ft.); other cells are both higher and lower. The voltage is better than 3.4 per cell (65 per cent voltage efficiency). The ampere efficiency is very high (for example, 97 per cent), for at the increased temperature, less chlorine is dissolved, and only a trace of chlorate forms.



FIGURE 33.—View of a cell room with type "S" cells, an improved diaphragm cell, of the Hooker Electrochemical Company. (By permission.) To left of center, note the large bus-bar connection to lower part of cell, and the $\frac{1}{2}$ -inch brine delivery line running at an angle to top of cell. Upper right, the large pipe line is for chlorine, the uppermost one, for hydrogen. Note also the different angles of caustic discharge pipes, and the small traveling crane, with free access to the tops of cells.

The cell has other features. Its construction allows the vertical removal of the upper section and of the cathode section; hence the cells may be placed close to each other, an economy in floor space. The horizontal entry of the brine starts the circulation of the anolyte, in order to relieve the working surfaces of the depleted layers of brine. The cell may be as large as needed to take a 10,000-ampere current; 7000 amperes is the usual size.

Nelson Cell. In the Nelson cell, as also in the Allen-Moore, Vorce, and several other cells, the cathode compartment is empty of liquor; the caustic solution, with residual salt, runs down the diaphragm and collects at the base. In the Nelson cell,¹⁰ steam is sent into the cathode space to maintain

⁹ U. S. Patent 1,862,245.

¹⁰ *Trans. Am. Electrochem. Soc.*, 35, 239 (1919), or U. S. Patents 1,149,210 (1915) and 1,149,211.

the temperature near 65° C. (149° F.). The form of the cell is again a narrow rectangular box set up as the Hooker cell is; the Allen-Moore has a similar outside appearance. There is only one row of suspended graphite anodes, and the usual size unit receives 1000 amperes; the current density is 50 amperes per square foot, half of that in the Hooker cell. The voltage is lower, averaging 3.7 volts. Among other advantages, this cell produces a very pure chlorine; for this reason it was chosen for the installation at Edgewood arsenal during the first World War ¹¹: 3500 Nelson cells furnished 100 tons of chlorine per 24 hours; the anodic ampere efficiency (for chlorine) was 90 per cent; the caustic liquor was maintained 10 to 12 per cent NaOH and 14 to 16 per cent NaCl.

Allen-Moore Cell. The Allen-Moore cell ¹² has usually 1200 ampere units, working with a voltage of 3.6; the cathodic current efficiency is maintained at 95 per cent over extended periods. The caustic liquor contains 8 to 10 per cent NaOH and about 12 per cent NaCl. The cell is constructed of concrete and cast-iron sides, and has in general the shape of a narrow rectangular box. The basic principle of the unsubmerged cathode, that is, of using an empty cathode compartment, was first proposed by the designers of the Allen-Moore cell.¹³

The cell described by L. D. Vorce ¹⁴ is cylindrical, and is said to furnish more caustic per square foot of floor space than any other cell. Another cylindrical cell used in Canada, and by the United Alkali Company of Great Britain, is the Gibbs cell,¹⁵ patented in 1907.¹⁶ The units are of 1000-ampere capacity, requiring 3.6 volts; the floor space occupied is small. The Gibbs cell ¹⁷ and the Vorce cell have an empty cathode compartment as have also the Allen-Moore and Nelson cells.

The Hargreaves-Bird cell produces sodium carbonate solution. The caustic soda primarily formed is changed to the carbonate at once by carbon dioxide and steam injected into the cathode compartment. The Griesheim cell has magnetic anodes, and solid salt is fed into the anode liquor.

CONCENTRATION OF THE CAUSTIC LIQUOR

The liquor flowing off from the cathode compartment contains both caustic and salt, for the diaphragm cells just discussed. The solution contains about 12 per cent NaOH and 12 per cent NaCl. It is concentrated in a double-effect evaporator,¹⁸ for example, and each boiling pan may have its own separator in which the salt is collected as fast as it separates from solution, so that the heating surface in the pan may always be swept by liquor. When a batch of cell liquor has been concentrated to 50 per cent NaOH only 1 per cent of salt remains in the solution. The suspension from pan and separator is pumped to a settler with Monel wire over a conical base; the salt settles on the wire, the caustic liquor collects in the cone. The liquor

¹¹ "The U. S. Government chlorine-caustic soda plant at Edgewood arsenal, Edgewood, Md.," Samuel M. Green, *Chem. Met. Eng.*, 21, 17 (1919).

¹² "The Allen-Moore cell in the pulp and paper mill," F. H. Mitchell, *Chem. Met. Eng.*, 21, 370 (1919).

¹³ *Trans. Am. Inst. Chem. Eng.*, 13, I, 11 (1920).

¹⁴ *Trans. Am. Inst. Chem. Eng.*, 13, I, 47 (1920), and U. S. Patent 1,286,844.

¹⁵ *Ind. Eng. Chem.*, 16, 1056 (1924).

¹⁶ Brit. Patent 28,147, also U. S. Patent 874,064.

¹⁷ In its original form, the Gibbs cell had caustic liquor in its cathode compartment.

¹⁸ Chapter 43.

passes to cooling tanks where any salt in suspension is carefully removed by settling. The 50 per cent liquor next reaches the cast-iron pots heated by coal or oil fire, where all the water is evaporated; the liquid anhydrous caustic, with perhaps 2 per cent NaCl, is removed from the pots by a centrifugal pump lowered from a crane.¹⁹ The liquid caustic is pumped to thin steel drums on low trucks; after cooling, the mass is solid. The weight of a caustic drum is generally 700 pounds net. Caustic soda is also marketed in crushed form, particularly for household uses; in flakes; and in the form of 50 per cent liquor, which is cheaper since the final evaporation in the caustic pot need not be performed.

The salt in the settlers is washed a number of times by liquors of decreasing caustic content; it is made up to a soft mush and pumped to the dissolver, re-entering the system with the raw salt solution.

In order to produce an absolutely iron-free caustic, some plants are now substituting for the pots continuous evaporators constructed of nickel.

THE MERCURY CELL

Castner Cell. In the Castner cell, the sodium formed at the cathode is dissolved in mercury to be changed to caustic in a subsequent operation. In

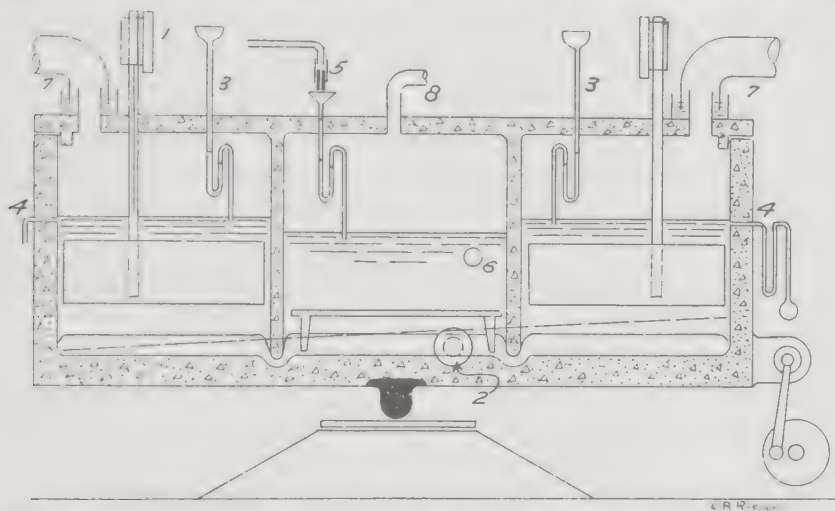


FIGURE 34.—Cross-section through the Castner cell, original type, showing the three longitudinal compartments, also shown in the next sketch. 1, anode; 2, cathode; 3, entry for brine; 4, exit for depleted brine; 5, water entry; 6, exit for caustic solution; 7, outlet for chlorine; 8, hydrogen escape. Note pivoting rib. When the cell tips to the right, the level of the mercury with respect to the cell walls is as shown by the dotted line, 4 to 4, 4 feet.

the original form of the Castner cell²⁰ the removal of the amalgam to the denuding chamber was by tilting, about once a minute, through a distance of one-half inch. Such a cell consists of a low slate box with three chambers; each of the two decomposing compartments have a graphite anode and mercury cathode; the chamber in the middle is the denuding chamber, with

¹⁹ For an account of the method of evaporation, compare *Ind. Eng. Chem.*, 16, 1057 (1924).

²⁰ *Electrochem. Ind.*, 1, 11 (1902).

an iron cathode suspended over the amalgam layer. The partitions between the chambers reach into grooves which are sealed with mercury but permit the amalgam to pass freely. The current enters at the anodes and leaves at the iron cathode. Brine is fed to the two decomposing compartments; water enters the denuding chamber while a solution of caustic, free from salt, leaves it; outlets for chlorine from the anode compartments and hydrogen from the

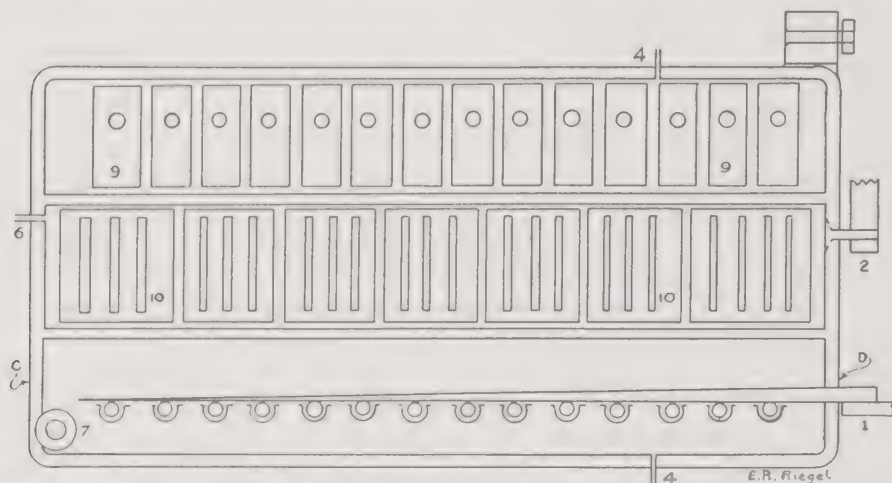


FIGURE 35.—Top view of the Castner cell, original type, with the cover removed from two of the chambers; the third chamber has its cover on, and shows the anode fingers coming to the bus bar. The numerals have the same meaning as in the previous sketch; in addition, 9 stands for the anode slabs; 10, the iron grids dipping in the mercury. C to D, 8 feet.

denuding compartment are provided. The units are fairly large, over 1000 amperes; the voltage is about 4; a liquor containing as high as 25 per cent NaOH is obtained. The concentration of the caustic is greatly simplified by the absence of salt.

Whiting Cell. The operation of a mercury cell appears simple and free from difficulties; but in reality very few plants have succeeded in operating the unmodified Castner cell. The chief difficulty, according to Whiting, is the incomplete removal of the amalgam from the decomposing compartment. In the modified cell²¹ the mercury is stationary during electrolysis; after 2 minutes, a valve opens which permits the amalgam to flow into a chamber below it, where it is denuded; the free mercury is lifted by a bucket wheel to a reservoir-trough just above the decomposing chambers, and is run in at 2-minute intervals. Five chambers make up one cell, so that the operation of the cell as a whole is continuous. A cell of five sections is 6 feet square, takes 1200 amperes at 4 volts per cell; the cathodic current efficiency is 90 to 95 per cent.

The Krebs mercury cell, as used in Sweden, is a long cell which takes up to 15,000 amperes. There are other European cells which take as high as 20,000 amperes.

The merit of the mercury cells is that they produce a caustic free from chloride.

²¹ *Trans. Am. Electrochem. Eng.*, 17, 327 (1910), also U. S. Patents 951,228-9.

THE BELL-JAR TYPE CELL

Billiter Cell. In the Billiter cell,²² the graphite anode is suspended in a bell-like housing, from which the chlorine is drawn off; the cathode consists of a number of iron rods slightly inclined from the horizontal; each rod is surrounded by a tight asbestos tube. At the edge of the jar, the rods and tubes rise upward; as the hydrogen is evolved along the rods, it travels upward, carrying with it the caustic liquor, which is delivered to a small receiving chamber in each cell, from which it is sent to the evaporators. The brine entry into the bell is such that the flow is toward the cathode, and as the caustic is carried out as fast as formed, it does not interfere with the passage of the current.

The estimated distribution of caustic soda sold in the open market is given in Table 8.

TABLE 8.—*Estimated Distribution of Caustic Soda Sales in the United States (in short tons)**

	1939	1940	1941
Soap	100,000	103,000	125,000
Chemicals	187,000	212,000	240,000
Petroleum refining	99,000	105,000	116,000
Rayon and cellulose film.....	196,000	230,000	270,000
Lye	44,000	48,000	52,000
Textiles	44,000	48,000	63,000
Rubber reclaiming	18,000	20,000	23,000
Vegetable oils	17,000	16,000	20,000
Pulp and paper	47,000	50,000	62,000
Exports	130,000	105,000	120,000
Miscellaneous	143,000	158,000	180,000
	1,025,000	1,095,000	1,271,000

* *Chem. Met. Eng.*, 49, February, 1942.

The average price for sodium hydroxide on the basis of 76 per cent Na_2O for 1939 was \$36.40. The figures for electrolytic caustic indicate a value per ton of \$35.50, while those for lime-soda caustic give \$37.20 a ton (Bureau of the Census).

Potassium hydroxide is produced in the United States to the amount of 13.856 tons (as 100% KOH). The production is, at least in part, by electrolysis, from the muriate, with hydrogen and chlorine as by-products. Potassium hydroxide is valued at \$132.50 a ton (Bureau of the Census).

BY-PRODUCTS OF ELECTROLYTIC CAUSTIC SODA

Hydrogen from the cathode chamber and chlorine from the anode chamber are the by-products of electrolytic caustic soda. The hydrogen is sometimes wasted; in some plants chlorine is burned in an excess of hydrogen to give a very pure hydrogen chloride which, dissolved in water, gives hydrochloric acid. It is likely that in the future, all the hydrogen will be utilized. The chlorine is the more important by-product of the two; it is produced at the rate of some 725,000 tons a year. The leakage of hydrogen into the chlorine must be avoided, for the two gases form explosive mixtures.

Liquid Chlorine. Gaseous chlorine is easily changed to a brown liquid; this circumstance has extended its usefulness considerably over that which the gas possesses. At 0° C. (32° F.), a pressure slightly over 39 pounds will

²² British Patent 11,693 (1910).

cause liquefaction; at -20°C. (-4°F.), slightly over 12 pounds is needed; at -33.5°C. (-28.5°F.), only a little over atmospheric pressure is required. A temperature of -20°C. may be obtained with an ammonia refrigerating system, brine or gas, while -40°C. (-40°F.) is obtained by a carbon dioxide system (Chapter 12).

The chlorine gas leaves the anode compartment warm and moist; under gentle suction it passes along a 3-inch stoneware line to a stoneware or quartz S-bend cooling system.²³ It next enters a stone box filled with scrap iron; ferric chloride forms, which is exceedingly hygroscopic and removes much of the water in the form of a strong ferric chloride solution.²⁴ More frequent than the ferric chloride box is a series of two short towers with large disks made up of coils through which water, the incoming brine, or refrigerated brine circulates; the condensate is run to a sewer. The partly dried gas may then be circulated in a battery of Cellarius vessels through which 66°Bé. sulfuric acid flows in the opposite direction (countercurrent principle). It next reaches a Nash²⁵ turbo-blower, whose multibladed impeller works in sulfuric acid held in an elliptical casing. For each revolution there are two compressions and two expansions of the working fluid, caused by the shape of the casing; the alternate compression and expansion move the gas. A pressure of 15 pounds may be obtained. The compressed gas is cooled in double-walled tubes, through the inner passage of which liquid carbon dioxide is expanding. The chlorine liquefies at a rapid rate, and is led to a steel storage tank. Any of the less compressible gases present as impurities, such as carbon dioxide, carbon monoxide, and hydrogen, are vented from the storage tank to bleach chambers.

The liquid chlorine is shipped in 50- and 100-pound steel cylinders, in single tank car units of 15 or 30 tons, and in 1-ton steel containers of which 15 are placed on a flat car.²⁶

The 1-ton unit is very convenient for making the bleach at the pulp or other mill, because the required quantity of milk of lime may be prepared and all the chlorine in the cylinder allowed to pass in without danger of wasting any. Calcium hypochlorite, $\text{Ca}(\text{OCl})_2$, and calcium chloride, CaCl_2 , are formed. All containers have one or two internal pipes, so that either the gas or the liquid may be drawn. If the gas is drawn, heat must be supplied to make up for the heat of vaporization, or else the process is very slow. It is more convenient and simple to use the liquid, mixing it directly with the milk of lime in a small mixing chamber²⁷; in that way the process of vaporization uses a part of the heat of reaction of chlorine on lime. In summer, this is important in keeping the temperature of the mixture below 40°C. ; above that point the calcium hypochlorite is unstable.²⁸

For the chlorination of municipal water supplies, and for any other chlorination away from the manufacturing plant, chlorine in the liquid form is preferred.

²³ *Chem. Met. Eng.*, **21**, 17 (1919).

²⁴ U. S. Patent 1,359,047.

²⁵ Nash Engineering Company, South Norwalk, Conn.; sketch in Chapter 41.

²⁶ Through a decision of the Interstate Commerce Commission the containers are considered as part of the car, and no freight is paid on them. See I. C. C. Docket 13895, 85 I. C. C. 728 (1924); Invest. & Susp. Docket 2456, 104 I. C. C. 196 (Nov. 9, 1925).

²⁷ U. S. Patent 1,481,106 to James H. MacMahon, assigned to the Mathieson Alkali Works (Inc.) of New York; the time required for the absorption of 1 ton of chlorine in 3 hours.

²⁸ The bleaching solution used in pulp and paper mills is 6°Bé. and contains 30 grams of available chlorine to the liter.

Chlorine is an essential war chemical, mainly indirectly, for it serves in the manufacture of a host of chlorine compounds which are essential to effective prosecution of warfare, the maintenance of healthful water supplies for civilian and soldier, for fire extinguishers and degreasing agents. The large production of 1939, 485,554 tons,* of which the portion sold (312,596 tons) was valued at \$33.25 a ton,²⁸ was exceeded in 1940, which was in turn exceeded in 1941 when 725,000 tons were produced. Of the 1941 total, 605,000 tons were produced as by-product of caustic soda, the balance as by-product of caustic potash, metallic sodium and magnesium, electrolytic sodium carbonate, and by the non-electrolytic nitrosyl chloride process.²⁸ The production in 1942 will undoubtedly be still greater.

Distribution of liquid chlorine sold in the open market for an average peace-time year follows:

Pulp and paper.....	65%	Sanitation	10%
Textile	20%	Miscellaneous	5%

Gaseous Chlorine and Bleach. Chlorine gas at the generating plant is used, without compression to the liquid, to make "bleach," and for the chlorination of organic substances such as benzene, toluene, pentane, and others.

Bleaching powder is the product of the interaction of chlorine gas and hydrated lime: $\text{Ca(OH)}_2 + \text{Cl}_2 = \text{CaOCl}_2 + \text{H}_2\text{O}$. The chloride of lime so formed, when dissolved in water, gives equal molecular parts of calcium chloride, which as far as bleaching is concerned, is useless, and calcium hypochlorite, which retains the total bleaching power of the original material



Chloride of lime or "bleach" must not be confused with calcium hypochlorite.

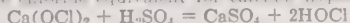
The chlorine absorption is performed either in a series of low-ceiling brick chambers, or in patent shelf absorbers which require little space. In either case the countercurrent principle is applied, the fresh gas meeting the richest bleach; the lean gas, the new hydrated lime. The bleach so prepared has been displaced to a considerable degree by (1) liquid chlorine, in mills and factories, (2) by calcium hypochlorite Ca(OCl)_2 , a stable material of high test, whereas ordinary bleach spoils after several months, and has a low test (35 per cent available chlorine). Available chlorine means chlorine evolved on addition of acid; 35 per cent available chlorine is a material which has the effectiveness of 35 parts of liquid chlorine. Pure calcium hypochlorite, by the laboratory test applied to all bleaching agents, rates 100 per cent available chlorine.²⁹

* Bureau of the Census.

^{28b} *Chem. Met. Eng.*, 49, Feb. 1942.

²⁹ The test for available chlorine in bleaching powder consists of acidifying in the presence of potassium iodide. The iodine liberated is titrated. It may be liberated by Cl_2 but also by oxygen.

Calcium hypochlorite contains 99.7 per cent available chlorine, yet only 50 per cent total chlorine; it is evident that a change in the method of designating the strength of bleaches is desirable. The most logical way would be to state the content of calcium hypochlorite, and this would also be the case for it happens that numerically the "available chlorine" present is almost the same as the calcium hypochlorite content. The chlorine equivalent for calcium hypochlorite is shown by the reactions:



Bleaching was explained formerly as oxidation; today it would be said to be the taking of electrons. A substance which accepts fragments (ions) which take up electrons is an oxidizing agent. Measured in that way, oxygen as well as chlorine is a bleaching agent, a fact already well known in an empirical way.

In 1939, the production of bleaching powder was 16,662 tons, valued at \$51.4 a ton; in 1923, for example, the production had been 146,974 tons.

High Test Hypochlorite [H.T.H.]. Calcium hypochlorite, $\text{Ca}(\text{OCl})_2$, essentially free from any other material, in the crystal form, is stable, and efforts to produce it in bulk have been earnest and successful.

One method for its manufacture is the chlorination of a lime slurry followed by the salting out of calcium hypochlorite by means of common salt (NaCl).³⁰ No organic solvent³¹ requiring later recovery is needed. The product may be made essentially 100 per cent $\text{Ca}(\text{OCl})_2$, but an additional operation is then required, so that the material actually marketed is 75 per cent $\text{Ca}(\text{OCl})_2$. It is therefore twice as strong as ordinary bleach; also, it does not spoil on standing, it is not hygroscopic, and when it is made up with water the solution is practically clear.

The latest and most successful method for making high test hypochlorite (H. T. H.) is the formation³² of the triple salt $\text{Ca}(\text{OCl})_2 \cdot \text{NaOCl} \cdot \text{NaCl} \cdot 12\text{H}_2\text{O}$ and its subsequent reaction with calcium chloride. The triple salt is made as follows: 40 parts NaOH , 37 parts $\text{Ca}(\text{OH})_2$ and 100 parts water are chlorinated at a temperature below 16°C . (60.8°F .), such as 10°C (50°F). This reaction (a) is: $4\text{NaOH} + \text{Ca}(\text{OH})_2 + 3\text{Cl}_2 + 9\text{H}_2\text{O} \rightarrow \text{Ca}(\text{OCl})_2 \cdot \text{NaOCl} \cdot \text{NaCl} \cdot 12\text{H}_2\text{O} + 2\text{NaCl}$. The comparatively large hexagonal crystals—the triple salt—separate and are centrifuged. In the meantime a special calcium chloride is prepared by chlorinating a milk of lime in these proportions: 74 parts $\text{Ca}(\text{OH})_2$, 213 parts water, 71 parts chlorine; the temperature is held at 25°C . (77°F .); (b) $2\text{Ca}(\text{OH})_2 + \text{Cl}_2 \rightarrow \text{Ca}(\text{OCl})_2 + \text{CaCl}_2 + 2\text{H}_2\text{O}$. Next, this solution is cooled to 10°C . (50°F .), the centrifuged crystals are added in the proportion required by the reaction (c) $2\text{NaOCl} + \text{CaCl}_2 \rightarrow 2\text{NaCl} + \text{Ca}(\text{OCl})_2$, and the suspension is agitated with paddles. On warming to 16°C . (60.8°F .), reaction (c) takes place and the whole sets to a rigid mass. The triple salt $\text{Ca}(\text{OCl})_2 \cdot \text{NaOCl} \cdot \text{NaCl} \cdot 12\text{H}_2\text{O}$ becomes $1\frac{1}{2}\text{Ca}(\text{OCl})_2 \cdot 2\text{H}_2\text{O}$, the dihydrate, 2NaCl and water. After drying in the vacuum, a material testing 65 to 70 per cent $\text{Ca}(\text{OCl})_2$ results. Such calcium hypochlorite as accompanied the calcium chloride is just that much more product. The NaCl content from (c) is not removed.

There are other high-test hypochlorites of calcium on the market, as for example Perchloron.

Sodium chlorite,^{32a} NaClO_2 , is a new commercial chemical which, combined with chlorine or hypochlorite, gives certain advantages in bleaching paper pulp. It is also finding use in connection with the bleaching and finishing of cotton, rayon and Celanese.

OTHER PATENTS

U. S. Patent 1,236,978 on a method for making high test calcium hypochlorite; 1,862,241, on cell construction; 1,862,245, on heat recovery in electrolysis; 1,996,769, manufacture of stable sodium hypochlorite; 2,040,717, 2,028,898, 2,030,694, purifying caustic solutions; 2,031,814, 1,922,591, manufacture of caustic soda; 1,609,757-8, process and apparatus for preparing liquid bleach.

³⁰ U. S. Patent 1,754,473 (1930).

³¹ U. S. Patents 1,481,039-40.

³² U. S. Patent 1,787,048, to Robert MacMullin and Maurice Taylor; see also U. S. Patents 1,787,051, 1,754,474, 1,754,475.

^{32a} "Sodium chlorite, properties and reactions," by M. C. Taylor, J. F. White, G. P. Vincent, and G. L. Cunningham, *Ind. Eng. Chem.*, 32, 899 (1940).

PROBLEMS

1. A 18 per cent Na_2CO_3 solution is made to react with a 28 per cent $\text{Ca}(\text{OH})_2$ slurry. (a) Assuming the reaction to be complete, what will be the concentration of the resulting caustic soda solution? (b) Consult the curve for conversion of sodium carbonate solution, and find the figure for 18 per cent Na_2CO_3 ; using this conversion figure, what will be the concentration of the caustic soda solution? For exact results, the weight of the non-converted Na_2CO_3 present in the caustic soda liquor must be computed and included in the solids which the liquor contains.

2. A batch of soda ash solution containing 19 per cent Na_2CO_3 is treated with the proper amount (use (a) the theoretical, (b) the amount required by a 94 per cent conversion figure) of a milk of lime containing a certain amount of water. How much water must the milk of lime contain, if the resulting caustic liquor is to be 41 per cent NaOH ? Find the answer for (a) and (b).

3. A plant causticizes 149 tons of soda ash (98.5 per cent Na_2CO_3) every day. The lime used is 94 per cent CaO . Allowing a 4.5 per cent excess of lime, and assuming that none is recovered, how many tons of lime will be required? What is the production of 50 per cent NaOH liquor, if the yield based on soda ash is 94 per cent?

4. A battery of 60 Nelson cells produces per day 10 tons of chlorine, at an anodic current efficiency of 93 per cent. The cathodic current efficiency is the same. How much caustic soda is produced at the cell? What is the current in ampere hours which passes through the cell if 1 ampere hour is required for 0.00329 pound of NaOH at 100 per cent current efficiency?

5. A plant has 18 tanks with capacity of 40,000 gallons each. The salt solution contained therein is 25 per cent NaCl , and has a specific gravity of 1.200. The plant produces per day 32 tons 850 pounds of 100 per cent NaOH , at 95 per cent yield. What is the storage capacity of the tanks expressed in days? In reality, the final product is 98 per cent NaOH for the diaphragm cell plants, and the remaining 2 per cent is salt (NaCl) and a small amount of carbonate; for the sake of simplicity, the purity is given as 100 per cent NaOH in this problem. Answer: 18 days.

6. The liquor from the electrolytic diaphragm cell contains 12 per cent NaOH and 12 per cent NaCl . For a production of 10 tons of solid caustic per day, how much salt will precipitate in the evaporator, if 2 per cent remains in the caustic? What decomposition efficiency does the cell liquor represent?

7. Verify the decomposition voltage for salt in solution to produce caustic and chlorine, given as 2.25 in the text. The heat of formation of NaCl is 96,400 gram calories; that of water, 68,370 gram calories, and that of caustic in solution, 112,700 gram calories. Compare Problem 4, Chapter 18.

8. It is desired to manufacture 75 tons of calcium hypochlorite testing 75 per cent "available chlorine" by the salting out method, the first method given under H.T.H. Find out how much lime will have to be used, how much chlorine, and how much calcium chloride in solution will be discarded. The relation may be assumed to be the theoretical ones.

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Atmospheric nitrogen is available in inexhaustible quantities. To convert this vast store of nitrogen into a raw material for the manufacture of indispensable fertilizers and peace-time as well as war-time explosives has been one of the major tasks of the chemist. He has discharged it brilliantly. Of the total compounds made or extracted for their nitrogen values, 75 per cent are "chemical nitrogen," or "air nitrogen" compounds.

Chapter 6

Synthetic Nitrogen Products—The Fixation of Atmospheric Nitrogen—Direct Ammonia, Cyanamide, Nitric Acid from Ammonia by Contact Catalysis

As long ago as 1780 Cavendish caused the combination of the nitrogen and oxygen in the air by means of an electric spark. The first practical large-scale manufacture of a nitrogen compound from atmospheric nitrogen was that of Birkeland and Eyde, at Nottoden, Norway, early in this century. In this process air is passed at a rapid rate through an arc spread out to form a flame. A previous attempt by Bradley and Lovejoy at Niagara Falls in 1902, using the arc method, had failed because the arc flame area was too small and because the gases were not removed from the reaction chamber fast enough. The Norwegian process benefited from the demonstrated faults in this installation.

The manufacture of synthetic ammonia was tried a little later, and succeeded first in the Haber process, in which a mixture of nitrogen and hydrogen is passed at moderately high temperature and under pressure over a contact catalyst, which causes a partial conversion of the elemental gases into ammonia. Several modifications of the process have been developed for making ammonia from the elements; they have been so successful that this process is now more important than all other synthetic processes combined. Ammonia salts are valuable fertilizers; moreover, if nitric acid is called for, ammonia may be oxidized with atmospheric air by the aid of a contact catalyst, so that the synthetic ammonia process may also produce from atmospheric nitrogen, in an indirect way, what the arc process furnishes directly.

An entirely different process for the fixation of atmospheric nitrogen is the calcium cyanamide process, which depends upon the fact that metallic carbides, particularly calcium carbide, readily absorb nitrogen gas to form the solid cyanamide. This substance as such is a fertilizer. By a further treatment it may be transformed into cyanide, by another into ammonia; but this ammonia is dearer than direct synthetic ammonia. The process was developed by Frank and Caro in Germany, in 1895-97, and has been introduced in many countries since that time, among others in the United States and Canada.

Another proposed process for binding the nitrogen gas of the air in the form of a chemical compound easily transported, which is what "fixation of atmospheric nitrogen" means, was the Bucher process which was intended

to produce cyanides, ferrocyanides, or hydrocyanic acid without using carbide. It is of no commercial importance at present.

Finally, nitrogen may be passed over metals at suitable temperatures to form nitrides which on treatment with steam yield ammonia. The best-known process which embodies this principle is the Serpek process, manufacturing aluminum nitride; it has been introduced in France but not in America.

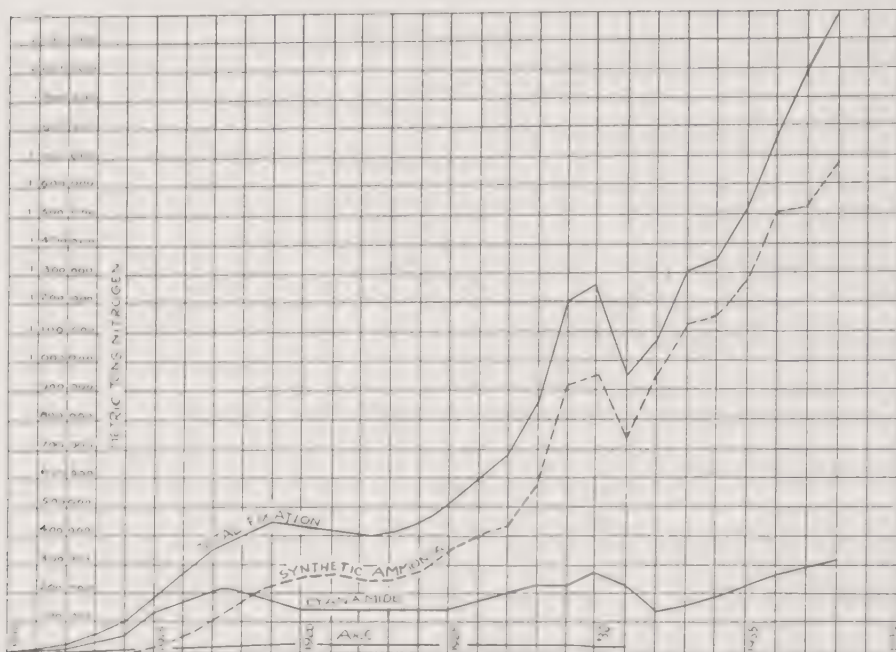


FIGURE 36.—The growth of atmospheric nitrogen fixation, for the world. No data is available for the years after 1933; and for the arc process, no reliable figures after 1931. (Based on information from the Division of Soil and Fertilizer Investigations, Bureau of Plant Industry, Department of Agriculture.)

The various processes with actual or potential values for the fixation of atmospheric nitrogen may be grouped together as follows:

a. The various arc processes in which ordinary air is passed at a rapid rate through a broad or long arc. The products are nitrates, nitrites, or nitric acid. This was the earliest method, but is hardly a factor any more.

b. The direct synthetic ammonia process, requiring nitrogen free from impurities, and pure hydrogen. The two gases mixed sweep over a catalyst while under pressure and at an elevated temperature; the product is ammonia, which may be further combined as a salt, such as the phosphate or the sulfate. By catalytic oxidation, the ammonia may be changed to nitric acid, and this in turn into nitrates. The great expenditure of electrical energy required in *a* is avoided in *b*.

c. The cyanamide process, which also requires fairly pure nitrogen, and calcium carbide, itself a product of the electric furnace. The material produced is calcium cyanamide. By steaming in autoclaves, ammonia is produced.

d. The cyanide and ferricyanide processes, in which nitrogen is passed into a vessel containing an alkali and coal mixed and heated.

e. The nitride process, in which nitrogen gas unites with certain metals. The product is treated with water, yielding ammonia.

The reason why the fixation of atmospheric nitrogen has been a difficult task is that elemental nitrogen is comparatively unreactive. It combines with only a few other elements, and then only under violent means, such as elevated temperatures.

The relative industrial importance of the three most important processes, d, e, and f, is shown in Figure 36. A glance suffices to tell that the synthetic ammonia process leads.

The capacity for the production of direct synthetic ammonia in the United States, on January 1934, was 341,350 tons (2,000 lbs.) of nitrogen annually, which was 10.6 per cent of total capacity of similar plants for the world. Germany was the leader, with 1,136,080 tons installed capacity.¹

The capacity for the United States has been greatly increased, to meet the national defense requirements, and may be taken at 100,000 tons more per year, beginning some time in 1942.

TABLE 9.—*World Production of Inorganic Nitrogenous Materials.*

	Quantity produced during the year ended June 30	
	Expressed in short tons of	
	Nitrogen*	
	1937	1938
Sulfate of ammonia		
By-product	472,900	453,000
Synthetic	758,400	843,300
Cyanamide	320,800	336,200
Nitrate of lime	197,300	214,900
Other forms of synthetic nitrogen†	938,100	1,026,200
Other forms of by-product nitrogen	58,400	54,000
Chilean nitrate of soda.....	227,100	246,900
Total world production.....	2,973,000	3,174,500

* Bureau of Chemistry and Soils, compiled from the British Sulphate of Ammonia Federation, Ltd., annual report. Fertilizers are included in this table under the final form as sold; for example, cyanamide, if converted into sulfate of ammonia, is included under "synthetic sulfate of ammonia," or, if into Ammophos, under "other synthetic nitrogen."

† Other forms of synthetic nitrogen mean: anhydrous liquid ammonia, Nitrochalk, Calnitro, urea, sodium nitrate, Ammophos, and others.

For the year 1935-36 the synthetic nitrogen products were 75.1 per cent, the by-product nitrogen compounds 17.3 per cent, and the Chilean nitrate 7.6 per cent of the total world production. For 1937-38, the corresponding figures were 76.1, 16.1, 7.8 per cent.

The world production capacity for synthetic nitrogen in 1936 was 3,700,000 tons a year.

No data are available for subsequent years, other than shown in the graph preceding, and in single items in this chapter.

Table 9 shows the world production for several years of nitrogen compounds in every form, Chile nitrate, by-product ammonia, synthetic ammonia and others.

THE ELECTRIC ARC PROCESS, USING AIR

The electric arc has been successfully applied to the fixation of atmospheric nitrogen: it was the first method evolved which permitted the fixation of such nitrogen. The main developments were the Birkeland and Eyde, in Norway; the Schoenherr, in Germany, and the H. and A. Pauling in Austria;

¹ A better table will be found in "Chemical Nitrogen," Report 114, U. S. Tariff Commission, (1937), tables 7 and 70. An earlier article is "World nitrogen developments in 1931," Chapin Tyler, *Chem. Met. Eng.*, 39, 44 (1932).

in each of these developments, the shape of the arc differs, and also the shape of the furnace. They agree, however, in the nature of the reaction: the union of atmospheric oxygen and nitrogen to form nitrogen oxide, NO , under the influence (chiefly thermal) of the arc; in all three, the reacted air with 2 per cent NO , must be withdrawn from the reaction zone as rapidly as possible, to prevent decomposition. This first oxide is oxidized further and absorbed in water or in lime, to give nitric acid of medium concentration in the first case, or calcium nitrate, a fertilizer, in the second case. Since the advent of synthetic ammonia, these furnaces have lost their importance, and probably only one of them is still operated, and even that is doubtful. One other reason for their failure is the high power requirement; 1 kilowatt year was required for the production of 600 kilos of nitric acid calculated as 100 per cent HNO_3 .²

The temperature of the flaming arc was estimated as 3200°C . (6000°F).¹

THE DIRECT SYNTHETIC AMMONIA PROCESS, BY CATALYSIS

If nitrogen and hydrogen are mixed and brought in contact with a substance such as specially prepared porous iron granules, at elevated temperature and under high pressure, they unite to form ammonia: $\text{N}_2 + 3\text{H}_2 \rightarrow 2\text{NH}_3 + 24 \text{ Cal}$. Even without the contact substances, the two original gases form ammonia in minute amount; this is of extreme importance, for a catalyst can only hasten the reaction which takes place to slight extent without it. That an increase in pressure should favor the formation of ammonia is due to the fact that 4 volumes of the original gases are changed into 2 volumes of the final gas.³ The temperature must be just high enough to allow high activity: beyond a certain value, an increase in the temperature retards the reaction by favoring the decomposition of ammonia. The amount of ammonia expressed in percentage by volume, for different pressures and temperatures, in the presence of a catalyst, is shown in Table 10.

TABLE 10.—Percentage Ammonia at Equilibrium.*

Ratio $\text{H}_2/\text{N}_2 = 3$.

Temp. °C.	Pressure (atm. absolute)						
	1	10	50	100	300	600	1000
200	15.30	50.66	74.38	81.54	89.94	95.37	98.20
300	2.18	14.73	39.41	52.04	70.96	84.21	92.55
350	0.90	7.41	25.23	37.35	59.12	75.62	87.40
400	0.41	3.85	15.27	25.12	47.00	65.20	79.82
500	1.21	5.56	10.61	26.44	42.15	57.47
600	0.49	2.25	4.52	13.77	23.10	31.43
700	1.05	2.18	7.28	12.87

* Compiled from publications of the Fixed Nitrogen Research Laboratory by Dr. Alfred T. Larson.

These values are obtained only if plenty of time is available, more time than can be allowed in a commercial application. A moderate percentage, but one quickly reached, is best suited to a commercial development, and the rapidity depends upon the nature of the catalyst. All the gases do not

¹ "The fixation of atmospheric nitrogen," Joseph Knox, New York, D. Van Nostrand Co., 1914. See also first edition of the present book.

³ This is in conformity with the principle of Le Chatelier, that "if an outside impulse is applied to any system in equilibrium, the system tends to arrange itself to absorb that impulse." In this case, the gases contract, in obedience to the pressure applied, by changing, to a greater extent, to the less voluminous ammonia.

react, but that is not necessary to render the reaction of commercial value; if the portion which has reacted is about 5 per cent, it can be removed and the remaining gases used over again. There are several systems which

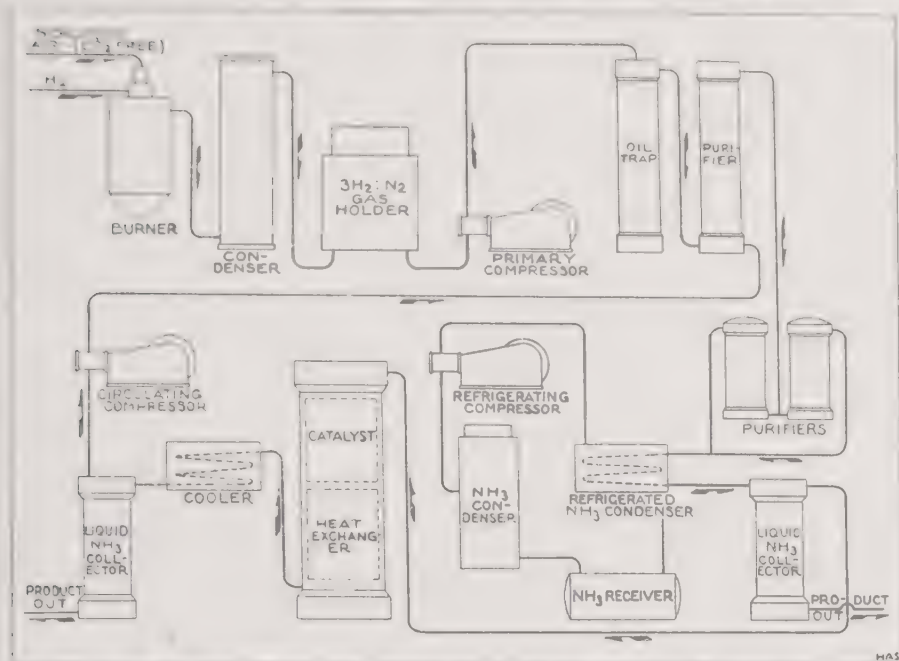


FIGURE 37.—Flow sheet for the direct synthetic ammonia process. The catalyst chamber and heat exchanger are combined in one tower about 40 feet high. On leaving the heat exchanger the gas deposits about half its ammonia content in the cooler at left of figure; the residual gas with its ammonia content is recirculated, and loses much of its ammonia in the refrigerated ammonia condenser at right of sketch. The recirculated gas is several times the make-up. (Drawn and reproduced by courtesy of The Mathieson Alkali Works, Inc., New York.)

depend upon this principle, the Haber in Germany, the Claude in France, the Casale in Italy, and the American in the United States.⁴ The Haber was the first to employ the direct synthetic method, and the others are indebted to it for the demonstration of the feasibility of the process on the commercial scale. The Claude, the Casale, and the American (or F. N.

⁴ The most important direct synthetic ammonia plants in the United States* with their capacity (January, 1934), in tons of 2,000 pounds of nitrogen are:

	Process	Hydrogen from	Capacity
Solvay Process Co., Hopewell, Va.	Own	Water gas	200,000
Du Pont & Co., Belle, W. Va.	Claude & Casale	Water gas	100,000
Shell Chemical Co., Pittsburg, Calif.	Mont Ceniz	Natural Gas	24,000
Mathieson Alkali Co., Niagara Falls	Nitrogen, Engineering Corporation	Electrolytic by-product	4,800
Midland Ammonia Co., Midland, Mich.	American	Electrolytic by-product	4,800
Pennsylvania Salt Co., Wyandotte, Mich.	Mont Ceniz	Electrolytic by-product	4,000
Du Pont & Co., R&H, Niagara Falls	American	Electrolytic by-product	3,000

* U. S. Tariff Commission Report 114, (1937).

The actual production for 1930-40 in the United States is reported to have been 245,000 tons of ammonia (S&I) and Fairbairn Investigations, Bureau of Plant Industry, U. S. Department of Agriculture, with the construction of two new plants, one at West Henderson, Ky., the other at Morgan, W. Va., the total capacity for direct synthetic ammonia will be well over 400,000 tons of nitrogen a year in 1942.

R. L.) systems are, however, independent developments of the general principle common to all four. They differ from the Haber and from each other in the pressure employed, in the method of removing the ammonia formed and in the preliminary manufacture and purification of the raw gases. Additional processes with characteristic features are the Fauser, and Mont Cenis.

The American system is the contribution of the Fixed Nitrogen Research Laboratory, Department of Agriculture, Washington, D. C. The details of this system have been made public without reservation, including the method of preparing the catalyst; it will therefore be presented first.

The American System. The method for the preparation of a mixture of 3 volumes of hydrogen and 1 volume of nitrogen differs with the size of the plant as well as with the system operated. In a small-scale installation, for experimental purposes, a simple way is to burn hydrogen from electrolytic cells which decompose water, in an excess of air. The oxygen of the air is fixed as water and this is removed by a cold-water condenser; the gas passing out of the condenser will consist of hydrogen excess, mixed with nitrogen. For full-scale installations, a mixed water gas, producer



FIGURE 38.—Hypercompressors for direct ammonia synthesis, Belle works, Charleston, W. Va. Each delivers compressed nitrogen plus hydrogen gas at the pressure of $7\frac{1}{2}$ tons per square inch. (Courtesy of E. I. du Pont de Nemours & Co., Inc., Ammonia Department, Wilmington, Del.)

gas, and steam is passed over suitable catalysts; the carbon monoxide reacts with steam to form carbon dioxide and hydrogen. The carbon dioxide is scrubbed out as described more fully under the Haber process. Hydrogen from any source (Chapter 19) and nitrogen from the liquefaction of air may be mixed in the proper proportions and used.

The Purifier. The several steps in the American system are illustrated in the flow sheet on page 115. The hydrogen was obtained in this case from

electrolytic cells, because of their compactness and ease of operation. A blower feeds the hydrogen to the burner; a cold-water condenser liquefies the water formed and a trap removes it. A compressor (4-stage) delivers it at a pressure of 300 atmospheres to the purifier, which is really a low-efficiency converter. (See Fig. 38.) A small amount of ammonia is formed, and condensed to the liquid state in the cold water condenser immediately following it. This condensed ammonia retains all impurities which the contact substance itself does not fix, so that the gas issuing from the condenser and separator is of the required purity. This gas is now fed to the high-efficiency converter, where the main conversion takes place; its contact material is maintained at a temperature of 475° C. (887° F.).

The Catalyst. The heart of the process is the converter, and the essential part of the latter is the contact substance. For the American system, exact knowledge of its nature is available.⁵ The high-efficiency catalyst consists of iron oxide granules containing the "combined promoters," potassium and aluminum oxides; the proportions are approximately 1 per cent potassium oxide and 3 per cent aluminum oxide, based on the weight of iron oxide. The preparation of the catalyst is as follows:⁶ Iron oxide, which may be prepared by burning pure iron in oxygen, is fused in an electric furnace; to prevent contamination, the hearth of the furnace is made of natural magnetite; the combined promoters are added to the fused mass, in the proportion given above. After the furnace has cooled, the oxide catalyst is removed, crushed, and sieved to give granules of uniform size. These are placed in the converter; the first portions of hydrogen gas in the regular mixture of nitrogen and hydrogen reduce the iron oxide to the metal; during this reduction, the granules probably become porous, which means the development of considerable surface. The explanation of the beneficent effect of the promoters is that they prevent sintering, and hence preserve the porosity.

The life of the catalyst is about 100 days, after which it must be replaced; raising the temperature to 500° C. (932° F.) greatly shortens the life of the catalyst mass.

The Converter. The converter for a 3-ton plant is an upright cylinder of chrome-vanadium steel 21 inches in diameter widening to 24 inches near the top which carries the removable head; the height of the cylinder is 7 feet. It is made of a single forging except for the head, which is held in place by nickel-steel bolts. The walls are 3 inches thick. For greater capacities, the dimensions are correspondingly larger (see under Claude process). The compressed gas enters the converter at the base and leaves at the top. The converter contains not only the contact substance but also the heat interchanger. In the reaction, $N_2 + 3H_2 \rightarrow 2NH_3$, heat is evolved; as much as possible of that heat is transferred to the incoming cold gases, so that the temperature at which the reaction is to take place may be attained without expenditure of fuel. This is not quite realized, and some supplementary heat must be supplied by means of a coil of resistance wire electrically heated and placed at the base of the interchanger, heating the gas as it enters the contact mass.

⁵ U. S. Patent 1,489,497 to Alfred T. Larson.

⁶ U. S. Patent 1,554,008; or *Ind. Eng. Chem.*, **17**, 971 (1925).

The interchanger is placed in the center of the converter, running through the whole height; around it is the contact mass, distributed in three concentric chambers of unequal sizes. A first narrow chamber surrounds the interchanger; a second, somewhat wider, chamber surrounds the first; the third similar chamber is the widest. The new gases first pass through the interchangers, to be heated. On leaving the central interchanger, the gas passes up the first chamber, down the second, and up the third, the down one coil of the interchanger and up the other to the outlet in the head of the converter. These various passages and the construction are shown in Figure 39. Each coil of the heat interchanger is double; through



FIGURE 39.—Converter for the American system for ammonia. *A*, space for the two double-walled coils of the heat exchanger; 1, first contact chamber in which the gas travels upward; 2, second chamber, with downward travel; 3, third chamber with upward travel. *P*, "Pyrex" glass reflector.

the central coil the cold gas flows; through the outer one the hot gas; no communication between the two gases is possible. The several contact chambers are formed by steel tubes.

The third chamber leaves a narrow passage between itself and the outer wall of the converter shell. It is through this space that the cold gas, which has entered at the bottom, streams on its way to the channels leading to the inner coil of the interchanger; this incoming cold gas keeps the shell relatively cool and therefore better able to resist stresses.

From the converter the gas enters the first condenser, which is water-cooled, where a part of the ammonia is liquefied. It then enters the circulating pump, lubricated by the liquefied ammonia in the gas. In the main condenser which follows, the cooling is by expanding ammonia, and here all the ammonia in the gas is liquefied. It is collected in receivers and pumped out of these by a liquor line. The receivers act at the same time as separators, the uncondensed gas passing out through a line which brings it to the converter entry. Mixed with fresh gas from the compressor, it undergoes partial conversion anew.

There is contraction from 4 volumes to 2 volumes for the portion of the gas which has reacted; in the American process this portion is 30 per cent.

If there is a loss of 10 per cent of the gas volume through leaks and through the loss of unconverted gases when purging the system of argon, there are required 100,000 cubic feet of the gas mixture (3H_2 and N_2) measured at 20°C . (68°F .) and atmospheric pressure for each ton of ammonia manufactured. In a plant producing 10 tons per day, which would still be a plant of moderate size, ten times that volume would have to be handled.

The product is obtained in the form of anhydrous ammonia of high purity; it is therefore ready for use in refrigerating plants using ammonia as working medium. In former days a special process was required to change the aqua ammonia made from the gas works liquor into the anhydrous liquid ammonia in steel cylinders. At one time, it was difficult to sell the ammonia from gas liquor for 30 cents a pound, anhydrous, and make a profit; now anhydrous ammonia is quoted at 5 cents (in tank cars). The market for such anhydrous ammonia is limited, and it is therefore invading the fertilizer market in the form of sulfate of ammonia. A tremendous market is opened, now that the ammonia is oxidized to nitric acid from which calcium nitrate and sodium nitrate are made, decreasing still further the importance of the Chilean deposits. In the near future, it is likely that all the nitric acid of commerce will be made in this way, and no longer from Chile saltpeter. The oxidation of ammonia to nitric acid is described at the end of this chapter.

The Haber Process. The catalyst in this system is promoted iron; the pressure is 200 atmospheres, and the temperature 550°C . (1022°F .). The conversion is comparatively low, about 8 per cent. The process is a complete success, nevertheless. The same company which developed the contact process for sulfuric acid, the Badische Anilin und Soda Fabrik, is also the company which fathered the Haber process; it is now (1937) part of the Interesse Gemeinschaft Farbenindustrie (I. G.), a huge combination of German chemical plants, with an installed capacity of over one million metric tons of nitrogen per year.

While the catalytic conversion is credited to Dr. Haber, the important problem of providing the raw gases cheaply and in the huge volumes required was solved by Dr. C. Bosch. Water gas,⁷ made by blowing steam over glowing coal or coke, and consisting essentially of equal volumes of

hydrogen and carbon monoxide, is mixed with producer gas⁷; the latter consists essentially of nitrogen, two parts, and carbon monoxide, one part. The mixed gases are mixed still further with steam, and this new mixture is sent through a hot catalyst which causes the water to react with the carbon monoxide to form hydrogen and carbon dioxide; the nitrogen remains unaffected (*see* Fig. 40). The catalyst used in this case is iron oxide containing small amounts of chromium and cerium. The proportions of the volumes are chosen to give at this stage hydrogen and nitrogen in the ratio by volume of three to one; but there is present the undesirable carbon dioxide and some carbon monoxide which has escaped the action of the steam. In order to remove carbon dioxide, the gases are put under pressure (50 atmospheres) and scrubbed with water, which at such pressure dissolves carbon dioxide readily; some remains, and is scrubbed out with a solution of caustic soda. The carbon monoxide is removed by scrubbing in ammoniacal copper formate while under 200 atmospheres pressure, which is the working pressure for the catalytic conversion. The cost of the gas mixture by this method is low, so that in the absence of hydrogen as a by-product it will probably be generally adopted.

TABLE 11.—*Sources for Hydrogen for the Production of Ammonia (World).**

Source	1926-27	1933-34
Water gas	89.0%	57.0%
Coke oven gas	3.0	25.0
Electrolysis, water	6.4	16.0
Other **	1.6	2.0

* Report 114, U. S. Tariff Commission, (1937), p. 41.

** "Other" means electrolysis of brine, fermentation, natural gas.

The converter⁸ is similar in principle to the one described under the American system. The proportion of the ammonia in the gas issuing from the converter is so low that mere cooling does not liquefy it sufficiently, and it must be removed by solution in water. The unconverted gases are freed from moisture and circulated through the converter with fresh gas, for further conversion. The ammonia, water which is the primary product, may be made to give up its ammonia gas very simply by means of continuous operating stills, or in stripping towers, described in Chapter 1, Part I.

The Mont Cenis Process.⁹ Similar to the Haber, and of more recent development, is the Mont Cenis direct ammonia process. Use is made of a highly active catalyst (an iron-cyanide complex), which is effective at a comparatively low pressure of 100 atmospheres, and at the temperature 400° C. (752° F.). The ammonia is obtained in liquid form at once.

The Claude System. The Claude system is distinguished by the high pressure used, higher than either the American (in the original form) or the Haber, namely, 900 atmospheres. The source of its hydrogen is coke-oven gas. There is present in coke-oven gas not far from 50 per cent hydrogen; removing it causes an increase in the B.t.u. value of the residual gas.

The hydrogen is separated from the other constituents by refrigeration. At the temperature of liquid air (− 180° C. or − 292° F.), only hydrogen remains a gas; it contains some methane and carbon monoxide which

⁷ U. S. Patent 1,202,995.

⁹ Proc. Intern. Conf. Bituminous Coal, 2nd Conf., Pittsburgh, Pa., 2, 202 (1928).



FIGURE 40.—Catalytic conversion of carbon monoxide to the dioxide by interaction with steam in the production of hydrogen for the ammonia synthesis, at the Luena works of the I. G. Each unit consists of a pre-heater, the lower section, and the reaction chamber above it. (Bourke-White Photo, from Pictures, Inc., Chrysler Building, New York.)

escape liquefaction. The nitrogen is obtained from liquid air;¹⁰ it is mixed with the impure hydrogen; the two are compressed to 900 atmospheres in an eight-stage compressor, and passed through a purifier containing a catalyst which changes the carbon monoxide, at the expense of some hydrogen, to methane and water. The water is removed, but not the methane, for it is harmless to the ammonia catalyst. The hydrogen-nitrogen mixture with its methane content enters a series of four converters; in each some ammonia is formed, which is removed by cooling before the gas enters the next converter. Issuing from the last converter, the unconverted gas contains 10 per cent of methane; all this gas is returned to the original hydrogen separator which produced the first slightly impure hydrogen. From this separator the methane, mixed with carbon monoxide, is removed in the liquid state and after gasification is burned under boilers. The portion of the gas mixture (H_2 and N_2) converted in the four converters is 80 to 85 per cent. There is no recirculation of the gas as in the American system.

To withstand the high pressure accompanied by the high temperature which varies between 500° and 650°C . (932° and 1202°F .), a special alloy is used: for example, 60 per cent nickel, 25 per cent chromium, 0.6 per cent carbon, the rest iron; or nickel 60.4 per cent, chromium 8.7 per cent, tungsten 2.5 per cent, carbon 0.4 per cent, and iron 25 per cent. The high temperature means that the catalyst loses its activity rapidly; the active mass must be replaced every 10 or 12 days. The change is made in 5 hours, thanks to the simple construction of the converter.

As advantages possessed by the Claude process may be listed: the handling of more material in a given reaction space compared with processes using lower pressures; a high space-time yield, made possible by the high temperature which favors rapidity of reaction (*see* Table 12); the fact that as the activity in the first converter drops somewhat, the second converter functions to a correspondingly higher degree, so that the over-all activity does not fall off.

With converters 27.5 inches in diameter and 11.5 feet high, 30 tons are made per day (900 pounds pressure); with converter tubes 39.37 inches outside diameter and 13.5 feet high, 50 to 100 tons may be produced. These sizes may be compared to Haber converters, 20 feet high and 4 feet outside diameter with 7-inch walls.

The Casale System. The original development under this system required a pressure of 750 atmospheres, and this has been raised still further. One converter is used,¹¹ and the gas is recirculated frequently. An important advantage of working at such high pressures is that water cooling is sufficient to remove the ammonia formed; another, perhaps more important, is the high conversion obtained, 40 per cent in a single passage through the converter. Except for the high pressure, this system resembles most the American system.

In 1934, there were 24 Casale plants in operation, of which 10 were in France. Of the 24, 9 were run on hydrogen from coke-oven gas, 10 on electrolytic hydrogen, 3 on water gas hydrogen.

¹⁰ Chapter 19.

¹¹ U. S. Patents 1,408,987 and 1,447,123, both with drawings showing construction of the converter.

The Fauser Process.¹² This process makes use of the oxidation of a portion of its ammonia in order to furnish its nitrogen for the direct ammonia synthesis. Ten per cent of the ammonia manufactured is mixed with air and passed to a platinum gauze converter. The oxides of nitrogen are scrubbed out and the residual gas saved. It consists mainly of nitrogen, but with a small amount of oxygen. It is mixed with hydrogen and passed over platinized asbestos, so that all the oxygen is changed to water. This latter is removed by cooling, and the purified gas is now pure nitrogen and hydrogen.

Table 12 permits comparison at a glance of the various systems for the direct synthesis of ammonia from the elements:

TABLE 12.—*Comparison of Synthetic Ammonia Processes.*

	Pressure atm.	Reported tempera- ture ° C.	Reported conversion maximum Per cent	Recircula- tion of un- changed gases	Catalyst
American	300	475	30	yes	Iron granules, "promoted"
Haber	200	550	8	yes	Iron granules, "promoted"
Claude	900	600	40	no	Iron granules, "promoted"
Casale	750	475	40	yes	Iron granules, "promoted"
Mont Cenis	100	400	40	yes	Iron-cyanide complex

The world installed capacity for direct synthetic ammonia production is distributed among the several processes as follows (1934): Haber-Bosch 35.2, Casale 14.9, Fauser 11.0, Claude 9.4, Imperial Chemical Industries 8.5, Mt. Cenis 8.0, N. E. Corp. 6.5, Gen. Chem. Co. 6.2, American .2.^{12a}

The preliminary work included a study of the content of ammonia in a mixture of hydrogen and nitrogen in contact with a catalyst at equilibrium. But it must be remembered that in practice the figure for ammonia formation attainable at equilibrium is not reached, because the gases are not allowed enough time to contact with the catalyst; the conversion must take place rapidly, for the gases stream by at a rapid rate.

To make comparisons between runs at different pressures and rapidity of flow, the concept of space velocity is used. Space velocity is the number of liters of exit gas, corrected to 0° C. (32° F.) and atmospheric pressure, which pass over 1 liter of catalyst space per hour. The space velocity for the direct ammonia processes is 40,000 on an average, with variations at the several plants.

Space-time yield is another useful value; it is the yield of ammonia per liter of catalyst per second.

It should be remembered also that as the pressure is increased, the volume of the reacting gases becomes smaller, so that a comparatively small catalyst bomb will handle a considerable volume of free gas. (See problems at the end of the chapter.)

A number of further statements regarding catalysis will be found in Chapter 25.

Shipments. Liquid anhydrous ammonia is transported in steel tanks of various sizes, the standard capacity being 50,000 pounds in a single unit. It

¹² A flow-sheet for the Fauser ammonia system will be found in *Chem. Met. Eng.*, 38, 628 (1931).

^{12a} (From Report 114, U. S. Tariff Commission.)

is also shipped in steel cylinders containing 25, 50, 100, and 150 pounds of ammonia.

Uses. The main use for ammonia is for fertilizer manufacture, chiefly in the form of ammonium sulfate, or as ammonium nitrate, phosphate, or urea. It serves as raw material for manufacturing nitric acid which, transformed into sodium or calcium nitrate, also finds its way into fertilizers.

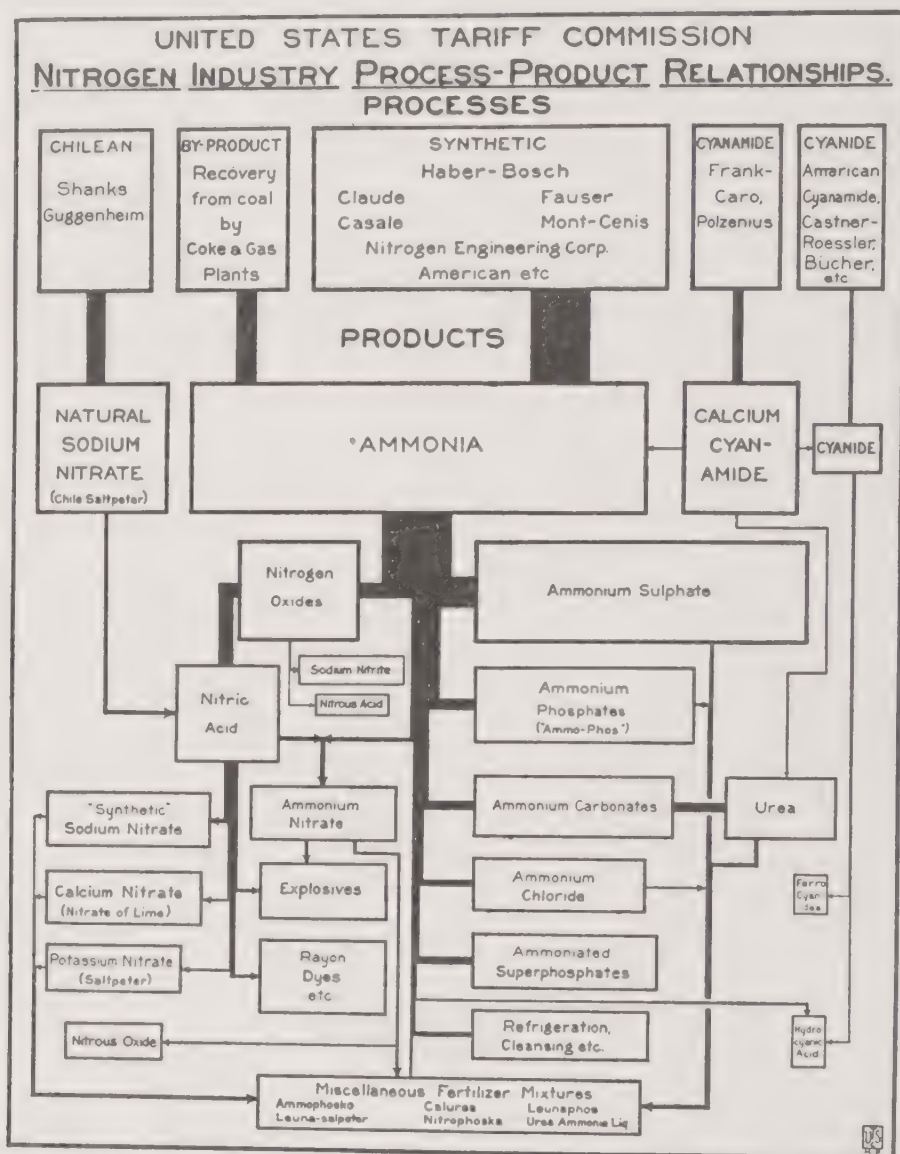


FIGURE 41.—Nitrogen industry process-product relationships for the world, (reproduced from report 114, U. S. Tariff Commission, 1937).

Ammonia serves the many uses to which an alkali may be put. Anhydrous ammonia is the most important refrigerating agent, because of its low cost and high thermodynamic efficiency. Ammonia is coming into use as a water purification agent, and as nitriding agent for steel. It is an important material in synthetic organic manufacturers, such as synthetic urea.

A rather novel use for ammonia is as a source of hydrogen, by passing anhydrous ammonia gas at atmospheric pressure over a catalyst heated to about 600° C. (1112° F.), such as an incandescent Nichrome wire coil. The great advantage lies in the fact that a 100-pound ammonia cylinder, easily transported, yields 3400 cubic feet of hydrogen (mixed with 25 per cent nitrogen).¹³

The Cyanamide Process. In the cyanamide process, ground calcium carbide¹⁴ is placed in iron drums each holding a charge of 4000 pounds, and fitted with a pipe connection so that nitrogen may be fed in. The center of the charge is heated by means of an electrically heated carbon rod and the nitrogen turned on; it is absorbed by the hot carbide, and the reaction evolves so much heat that the carbon rod may be removed after a few minutes; the heat of reaction is sufficient to keep the mass at the reaction temperature. The reaction $\text{CaC}_2 + \text{N}_2 = \text{CaCN}_2 + \text{C}$ takes place and continues until, after 40 to 60 hours, all the carbide is transformed into crude calcium cyanamide. A solid mass results which, after cooling, is crushed, powdered, and sprayed with water to destroy any unchanged carbide, then with oil to diminish its dustiness. The black powder resulting from the operation contains 60 per cent CaCN_2 and is used as ingredient in mixed fertilizers without further treatment.

In a round-about way, nitric acid may be produced from cyanamide, by first making ammonia. The cyanamide is placed in autoclaves 21 feet high and 6 feet in diameter and treated with steam¹⁵; the ammonia generated may later be oxidized by the hot platinum grid contact method, and the nitric oxide absorbed in water. The ammonia itself may be used in various ways, for instance, to make anhydrous ammonia for refrigeration, sulfate or phosphate of ammonia for fertilizers, and nitrate of ammonia for explosives. The reaction in the autoclave is $\text{CaCN}_2 + 3\text{H}_2\text{O} = 2\text{NH}_3 + \text{CaCO}_3$.

The nitrogen fed into the carbide charge is made by liquefying air and boiling off the nitrogen in fractionating columns.¹⁶

Until the advent of the direct synthetic ammonia process, the cyanamide process held a place of importance in the field of fixation of atmospheric nitrogen; at the present time, it seems more likely that it will retain its importance as a process fixing atmospheric nitrogen in the form of the fertilizer ingredient calcium cyanamide, but not as a producer of ammonia and ammonium salts.

By fusion with salt, carbon, and a little carbide, calcium cyanamide may be transformed to sodium cyanide, which in solution is valuable for the extraction of gold and silver from their ores. (See also Chapter 18.)

Calcium cyanamide is also the starting material for a number of organic substances, such as guanidine, urea, dicyandiamide, which have become of great importance.

The installed capacity for calcium cyanamide in Niagara Falls, Ontario, Canada, was (1934) 80,000 tons of nitrogen per year, which is 14.5 per cent

¹³ "Ammonia as a source of hydrogen and nitrogen," J. F. T. Berliner and G. W. Burke, *Trans. Am. Inst. Chem. Eng.*, 25, 42 (1930).

¹⁴ Chapter 17.

¹⁵ A complete diagram of a plant for generating NH_3 from calcium cyanamide will be found facing p. 264, in "The atmospheric nitrogen industry," Bruno Waeser, trans. by E. Fylenan, Philadelphia, P. Blakiston's Sons & Co., 1926.

¹⁶ Chapter 19.

of the world total cyanamide capacity; Germany had 36.7 per cent, Japan 12.9 per cent of it. There is no production in the United States. In 1917 there were imported from Canada into the United States 118,363 long tons of calcium cyanamide, an amount smaller than the corresponding amounts of the previous three years.

The Bucher Process. Soda ash mixed with iron and carbon may be heated in a current of nitrogen, to produce sodium cyanide and a ferric cyanide.¹⁷ The operation of an experimental plant using this process was discontinued about 15 years ago.

The Serpek Process. Certain metals at elevated temperature unite readily with nitrogen while heated to form nitrides, which in a subsequent treatment with steam give up all their nitrogen in the form of ammonia. The best known of these processes is the Serpek, developed on a fair scale in France. It consists of passing a mixture of crude alumina (bauxite) and coke through a rotary furnace one way, while nitrogen (producer gas) passes the other way. The furnace is heated externally by electrical means to a temperature of 1800° C. (3272° F.). The operation is continuous:



On treatment with dilute alkali, ammonia is formed, together with very pure alumina $\text{AlN} + 3\text{H}_2\text{O} = \text{Al}(\text{OH})_3 + \text{NH}_3$. If the demand for the by-product were greater, this process would undoubtedly find more general application.¹⁸

NITRIC ACID FROM AMMONIA

A considerable portion of the ammonia produced by the direct synthetic process is changed to nitric acid by catalytic oxidation. For several years in the past decade, essentially all the nitric acid made in the United States was so produced, so that the need for Chilean nitrate had passed. Similarly in Europe, especially Germany, the absolute need for Chilean nitrate has become a thing of the past. The French government plant at Toulouse has a capacity for 80,000 metric tons of sodium nitrate per year, in addition to a large production of ammonium sulfate and other fertilizer materials. Now that the pressing war demand must be met, new plants for the oxidation of ammonia have been installed and several more are being built. Also, the importation of Chilean nitrate, which had stopped, has been renewed, so that there may be available both for military purposes and for agriculture as much of this nitrogenous material as possible.

Oxidation of ammonia by air with subsequent absorption of the nitrogenous gases in water is performed at ordinary pressure, or under a pressure of 100 pounds. Each has certain advantages. In either case, the principle of the method is that ammonia gas and air mixed (11 per cent NH_3), passed through a fine wire gauze of activated platinum raised to glowing heat, combine to form nitric oxide (NO) and water. The first reaction is $4\text{NH}_3 + 5\text{O}_2 = 4\text{NO} + 6\text{H}_2\text{O}$. It takes place at a rapid rate, with a 95 per cent conversion, or better; the time of contact is 0.0014 second. The wire

¹⁷ "The fixation of nitrogen," John E. Bucher, *Trans. Am. Inst. Chem. Eng.*, 9, 335 (1916). For a recent study of this process, see *Ind. Eng. Chem.*, 18, 43 (1926).

¹⁸ "The fixation of nitrogen as aluminum nitride," H. J. Krase, J. G. Thompson, and J. Y. Yee, *Ind. Eng. Chem.*, 18, 1287 (1926), contains all the older references.

is of the fineness of silk. Activation is done by passing a mixture richer in ammonia through the gauze while it is electrically heated. The preliminary activation may be left out, and the gauzes allowed to activate themselves during the first few hours of the run. In the Jones-Parsons converter,¹⁹ the cylinder is 9 inches in diameter and 13 inches on the side; it is suspended so that its long axis is vertical, and its lower opening is closed by a silica piece. The gas mixture enters from above and streams downward through the screen. The wire is 0.003 inch in diameter, while the gauze has 80 meshes to the inch. The preheated gases react and gradually raise the temperature of the gauze to 1025° C. (1876° F.), for the reaction is exothermic. The walls at red heat send back heat by radiation to the gauzes, helping the maintenance of the temperature. The capacity of this converter is 2½ tons of 100 per cent HNO₃ per day, with a conversion of 96 per cent.

The latest design has an aluminum mixing chamber, in order to avoid pre-ignition (*see* Fig. 42.) Other designs have a flat horizontal gauze.

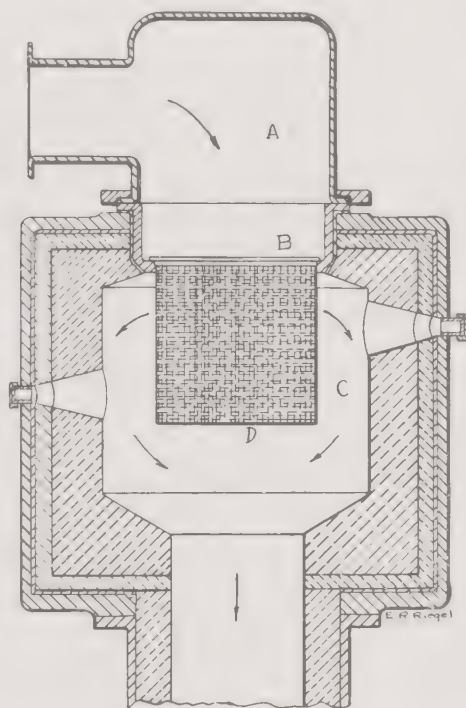


FIGURE 42.—The Chemico ammonia oxidation converter. A, mixing chamber, of aluminum; B, gauze holder, of nickel; C, platinum gauze; D, solid silica plate. (Sketched through courtesy of the Chemical Construction Corpn., New York.)

The oxidized gases leaving the converter pass through heat exchangers, cooling pipes of chrome steel, and reach the absorption towers fed with water and weak acid, on the counter-current principle. Here, or in some other specially provided space, the oxidation of the nitric oxide to the dioxide takes place, $2\text{NO} + \text{O}_2 = 2\text{NO}_2$. This is a slow reaction; cooling the gases favors it. In the absorption towers, the reaction $3\text{NO}_2 + \text{H}_2\text{O} = 2\text{HNO}_3 + \text{NO}$ takes place. The NO formed is oxidized to NO₂ again, in the towers,

¹⁹ *Ind. Eng. Chem.*, 19, 789 (1927).

and is gradually all absorbed. The nitric acid from the absorption tower is 50 per cent HNO_3 .

Low Pressure System. All the foregoing remarks apply to the low pressure system, which operates at atmospheric pressure. Its main advantage is that the absorption system may be built of stoneware, masonry, or granite instead of chrome iron, so that the installation cost is less per pound of nitric acid produced; the installation cost for chrome iron pressure system may, however, be no more. In the low pressure system, the general operation is simpler.

High Pressure System. The high pressure system is operated at various pressures; as an example, 100 pounds may be taken.²⁰ The absorption system in this case must be of chrome-iron alloy²¹ to withstand the pressure; but a number of advantages are gained. The capacity of the apparatus is high. A plant producing 25 tons of acid (as 100 per cent HNO_3) per day consists of one converter delivering finally into a plate tower 5½ feet in diameter and 40 feet high.²² For the same production, the atmospheric plant requires four burners and 10 towers. The plate tower is cooled at every shelf (with well water), for not only increased pressure but also low temperature favor capacity and strength of acid. In the high pressure plant 61 per cent HNO_3 is produced, whereas the atmospheric system furnishes 50 per cent acid. The conversion is 93 per cent.

Some of the finer points must be mentioned. During the conversion, there is a loss of platinum, amounting to 5 per cent per month for low-pressure operation. When the reaction temperature is raised, which leads to higher conversion efficiency, the loss is increased. With platinum-10 per cent rhodium, the loss is halved.²³ The loss per pound of ammonia burned is not affected by pressure.

To obtain high conversions, the ammonia must be freed by distillation with filtration of the gas, from the very minute amount of oil it contains; the air must be filtered.²⁴

For many purposes, 50 per cent or 60 per cent HNO_3 is satisfactory as to strength; for nitrations of all kinds, it must be stronger. This necessitates an additional operation.

Concentrated Synthetic Nitric Acid. The 50 or 60 per cent HNO_3 is concentrated to 98 or 95 per cent by adding 66° Bé. sulfuric acid, and distilling from a retort; the nitric acid passes out, while the water is retained by the sulfuric acid, which becomes 75 per cent acid. This is concentrated in one of the standard sulfuric acid concentrators. Instead of a retort, a Pauling tower may be used, fed with the mixed acid at the top, and steam at the bottom. Another apparatus is the continuous retort system, "Chemico," consisting of a series of steam-jacketed, acid-proof iron pipes. (Read also "Salt Cake" in Chapter 3, and "Nitric Acid" in Chapter 2.)

Synthetic sodium nitrate: The nitric acid from ammonia oxidation may

²⁰ *Ind. Eng. Chem.*, **23**, 860 (1931).

²¹ 17% chromium, less than 0.15% C.

²² A diagrammatic flow-sheet of a pressure plant will be found in reference 20.

²³ U. S. Patents 1,706,055.

²⁴ Reactions producing elemental nitrogen prevent perfect conversions, such as, $4\text{NH}_3 + 3\text{O}_2 = 2\text{N}_2 + 6\text{H}_2\text{O}$, $4\text{NH}_3 + 6\text{NO} = 5\text{N}_2 + 6\text{H}_2\text{O}$; $2\text{NH}_3 \rightleftharpoons \text{N}_2 + 3\text{H}_2$, $2\text{NO} \rightleftharpoons \text{N}_2 + \text{O}_2$.

be neutralized with soda ash, to give synthetic sodium nitrate. Crude residues and comparatively weak lots of acid may be utilized in this way.²⁴⁵

Sodium nitrite is made by absorbing nitrogen oxide in soda ash solution; the method involves mixing mother liquor with soda ash solution and treating with the gas. The nitrate-nitrite is crystallized out.²⁴⁶ By regulating the air ratio a composition close to the theoretical N_2O_3 may be secured and comparatively pure nitrite obtained. It is purified by crystallization.

An older method for making sodium nitrite is given in Chapter 31.

Fausser Process²⁵ for Concentrated Nitric Acid from Ammonia in a Single Step. It is highly desirable to find a way to manufacture the strong acid directly from the gases issuing from the converter, avoiding the concentration by means of sulfuric acid. This is accomplished in the Fausser process. The reacted gases leaving the converter are cooled rapidly, in order to condense and trap away the water of reaction. The nitric oxide (NO) first formed remains, for the greater part, unoxidized under these conditions. It passes to an oxidation tower, where NO_2 and N_2O_4 form, then to a cooling tower operated at -10°C . (14°F .) and 10 atmospheres; in addition to the gases, the proper amount of dilute nitric acid is introduced at the top of the tower. There passes out at the bottom a mixture of liquefied N_2O_4 and dilute acid, which is pumped into an autoclave. After the charge is in, the temperature is raised to 70°C . (158°F .), and oxygen, under a pressure of 50 atmospheres, is introduced. In 4 hours, the reaction $2\text{N}_2\text{O}_4 + 2\text{H}_2\text{O} + \text{O}_2 = 4\text{HNO}_3 + 18.8\text{ Cal.}$, has gone to completion; the acid is 98 per cent or better.

OTHER PATENTS

U. S. Patents 1,845,050 and 1,845,068, methods and apparatus for conducting exothermic gas reactions; the incoming gas mixture while being preheated, is in contact with a preliminary amount of catalytic mass. 1,855,040, in which two separate reaction bombs are used, one for purifying and one for producing. Each of these 3 patents has drawings showing construction of converters suitable for the ammonia synthesis. 2,052,326, catalytic converter and ammonia synthesis; 2,010,235, catalytic oxidation of ammonia; 2,018,760, catalyst for ammonia oxidation and the like; French Patent 848,694, on ammonia synthesis; Russian Patent 52,384, on iron catalyst; U. S. Patent 2,234,169, converters for ammonia synthesis or oil hydrogenation, to Eugene J. Houdry and Raymond C. Lassiat. On oxidation of ammonia, U. S. Patent 2,231,202, and Canadian Patent 394,134.

PROBLEMS

1. A direct synthetic ammonia plant produces 1 ton of NH_3 per hour in a catalyst chamber with a catalyst volume of 10 liters. Assuming perfect conversion, and no losses, what is (a) the weight of hydrogen needed; what is its volume at 0°C . and 1 atmosphere? Using the simple gas laws, what is (b) the volume of the same amount of hydrogen as for (a), for the following conditions: 100°C . and 1 atm.; 100°C . and 100 atm.; 100°C . and 1000 atm.; 300°C . and 1000 atm.? The formula to be used is $pv = NRT$, N is the gram mols, R is the gram molecular gas constant and equals 0.082154; T is absolute temperature; p is given, in atmospheres; with these figures, the answer will be in liters. $3\text{H} = 3.024$; $\text{NH}_3 = 17.032$.

Answer: (a) 1,791,900 liters; (b) 3761.1 liters at 300°C . and 1000 atm.

2. The volumes computed in 1 give a good representation of the enormous decrease in volume due to the high pressures, in spite of the high temperature. These volumes are not correct, however, because hydrogen does not follow the gas law exactly. In order to find the true volume, compressibility coefficient must be used, which rest on experiments. By means of the compressibility coefficient, the volume in cc. for one

²⁴⁵ For sodium nitrate hard pellets, see Chapter 8.

²⁴⁶ U. S. Patent 2,032,699; the proportion of NO_2 and NO formed from the NO and O_2 and N₂ mixture leaving the platinum converter depends upon the rapidity of cooling.

²⁵ Chem. Met. Eng., 39, 430 (1932), with a diagrammatic flow-sheet.

gram of the gas is computed; knowing the weight, the total volume may be obtained readily.†

	Hydrogen	Nitrogen	$N_2 + 3H_2$	Ammonia
0° C. and 1 atm.	1	1	1	1
100° C.; 1 atm.	1.3660	1.3669		1.379
100° C.; 100 atm.	1.4356	1.4121	1.4362	*
100° C.; 1000 atm.	2.0844	2.4948	2.1870	*
300° C.; 1000 atm.	2.8157	3.3203	2.9504

* The critical temperature for NH_3 is 132.4° C., the critical pressure 115 atmospheres, explain why the data are missing.

The compressibility factor is used as follows: For 100° C. and 1000 atm., for hydrogen its value is 2.0844. Then

$$v = \frac{2.0844}{1000} \times \frac{22,428}{2.016} = 23.20 \text{ cc. per gram.}$$

Compute the volume for hydrogen for the conditions stated in Problem 1, and list the results opposite the results from 1.

Answer: For hydrogen, for 300° C. and 1000 atm., corrected: 5045.6 liters.

3. Perform the same computations for nitrogen, and for the mixed gases as represented by $N_2 + 3H_2$. The apparent molecular weight for this mixture is 8.516.

4. With a conversion of 40 per cent, the amount of hydrogen computed above in 1 and 2 is only a part of a larger total. What is this total? What is the volume of the exit gases, expressed for standard conditions (the ammonia assumed to remain gaseous)?

5. In a regular run for direct ammonia, the space velocity is 39,600. The hydrogen-nitrogen gas mixture is 3 hydrogen and 1 nitrogen. The catalyst volume (apparent volume) is 10 liters. The conversion is 40 per cent, and there are no losses. In which period of time will 1 ton of NH_3 be made? And in that period, what is the volume of raw gases which must be sent into the converter, in order to give the performance specified? Express this quantity for standard temperature and pressure (0° C. and 1 atm.); find its volume for 300° C. and 1000 atm., which will be the working conditions, in two ways, first according to the simple gas laws, second, using the compressibility coefficients given under Example 2.

Note: The apparent molecular weight of the $3H_2 + 1N_2$ gas mixture is 8.516.

Answer: 12 hours is the period of time.

6. In the Fauser process for direct ammonia, the reaction for preparing the needed nitrogen is $2NH_3 + 2.5O_2 = 2NO + 3H_2O$. The oxygen brings with itself the nitrogen which air contains. Is the statement and the figure of 10 given in the text correct, and is it per cent by volume or by weight which is meant?

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Until a very few years ago, North America mined more phosphate rock than any other continent. This is no longer so: North America is now out ranked in this respect by Africa. Man eats lime and phosphates in order to have the mineral materials for his teeth and bones. The phosphate pebble deposits are the legacy to man from the prehistoric animals, who perhaps did not live in vain, since thanks to their having lived, there is a supply of this essential element (phosphorus) at man's disposal. The same phosphate radicals which perform so useful a function in man's body, performed the same function for the humble dwellers of the earth in prehistoric time.

Chapter 7

Phosphates, Phosphoric Acid, Baking Powders

The phosphates for fertilizers, phosphoric acid and its products, and for phosphorus come from two sources: bone ash, and mineral deposits, both more or less pure tricalcium phosphate. Bone ash is purer than the mineral material, as one would expect, and serves for making phosphoric acid and monocalcium phosphate for baking powders, as far as its limited supply allows; and the mineral phosphate is the material for superphosphate, of which 4,385,971 tons were manufactured in the United States in 1940.

New deposits of mineral phosphate material have been discovered gradually in the course of the past 50 years; they are indicated by the corresponding production figures listed in Table 13.

TABLE 13.—*Main Producing Countries of Natural Phosphates in the World, in Metric Tons (U. S. Bureau of Mines).*

	1938	1939	1940
Tunisia	1,934,200	1,608,045
Morocco (French)	1,447,544	1,491,754
Algeria	584,452	450,000
Egypt	458,404	547,538
Tanganyika Territory	1,934,200	1,608,045
Nauru and Ocean Islands	1,184,816	1,244,170	1,267,044
Christmas Island, Straits Settlements (exp.)	162,425	177,972
Curacao	99,283
Makatea Island	102,941	160,680
U. S. S. R. in 1936	920,000
United States of America, sold or used	3,799,253	3,817,368	4,066,943

Within the United States, the mineral phosphate deposits, in the order of their commercial utilization, are: Florida land pebble (30 to 36 per cent P_2O_5), Tennessee brown rock (25 to 37 per cent P_2O_5), Florida hard rock (25 to 37 per cent P_2O_5), Tennessee blue rock (27 to 33 per cent P_2O_5), Western rock (26 to 32 per cent P_2O_5), soft and waste pond phosphates of Florida (15 to 35 per cent P_2O_5), South Carolina phosphate (30 per cent P_2O_5).

As the percentage figures for the phosphoric acid content (P_2O_5) indicate, there is a variation in the quality of the phosphate deposits. High-grade rock contains 70 to 80 per cent tricalcium phosphate; the impurities are mainly clay, limestone, sand and calcium fluoride.¹ The Florida² land

¹ Ratio of fluorine to phosphoric acid is constant, for a given deposit; see *Chem. Met. Eng.*, 21, 1253 (1929).

² One district lies along the Charlotte Harbor and Northern Railway which runs through Charlotte, De Soto, Hordee, and Polk counties; another is near Dunellon, in Marion County.

pebble is high grade, and is found on the bottom and along the banks of rivers and lakes. The pebbles on the bottom of rivers are gathered by scoops, washed and dried in rotary cylinders; the banks are mined hydraulically and at the same time the pebbles are washed free from clay and earth, then dried. Tennessee³ brown rock is also high grade, but has a greater impurity of iron and alumina⁴, both the brown rock and blue rock are actively exploited. The washing is done in a variety of ways, among others by stirring the crushed rock with water and running off the lighter clay suspension. The western rock is somewhat lower in grade, and contains much organic matter (7 per cent); by roasting the rock before using it for superphosphate, the phosphoric acid content is raised, and a waste of sulfuric acid is avoided. All phosphate rock deposits occur in beds a few feet thick; thus for Tennessee, the average is 6 to 8 feet. The Tunisian mine near Gafsa and the Algerian⁵ deposit near Tebessa have beds varying from 2 to 10 feet in thickness. Less extensive deposits occur in Spain, and in the Somme region, in France.

Finely ground phosphate rock has been used for direct application to the soil, but the amount is slight compared to superphosphate tonnage.*

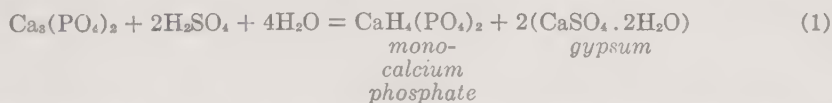
A defluorinated phosphate is being produced for use in animal feeds to replace bone meal.†

The production by states is shown in Table 14.

TABLE 14.—*Production of Phosphate Rock in the United States (1940)*
in Long Tons (U. S. Bureau of Mines).

Florida	2,845,012
Hard rock	22,367
Soft rock	41,845
Land pebble	2,780,800
Tennessee	994,361
Idaho	99,088
Montana	64,239
U. S. total	4,002,700

Superphosphate. Superphosphate is made by the action of chamber acid 50° to 55° Bé., corresponding to 62 to 70 per cent H₂SO₄, on tricalcium phosphate, the essential constituent of phosphate rock. The amount of acid is so regulated that the monocalcium phosphate is formed, soluble in water:



Calcium sulfate in the form of gypsum remains mixed with the monocalcium salt, and it is this mixture which constitutes superphosphate. A

³ Maury, Hickman, and Lewis counties.

⁴ These impurities may be reduced by applying flotation methods; K. D. Jacob, *Ind. Eng. Chem.*, 23, 15 (1931); in superphosphate, iron and aluminum oxides favor reversion.

⁵ *Chem. Abstracts*, 19, 1551 (1925).

* U. S. Department of Agriculture Yearbook, 1939, p. 513. See also "Availability of phosphate rocks in soils of varying degrees of acidity," by R. P. Bartholomew, *J. Am. Soc. Agronomy*, 29, 293 (1937).

† Minerals Yearbook, 1940; see also Technical publication 695, "Phosphate fertilizers by calcination process—volatilization of fluorine from phosphate rock at high temperatures," by K. D. Jacobs, D. S. Reynolds, and H. L. Marshall, *Am. Inst. Min. Met. Engineers* (1936); and "Report on phosphoric acid, availability of calcined phosphate and other new phosphatic materials as determined by chemical and vegetative tests," by Wm. H. Ross and K. D. Jacob, *J. Ass'n. Official Chemists*, 232-249 (1937).

certain amount of dicalcium phosphate, CaHPO_4 , insoluble in water, is formed also, and is determined in the analysis by virtue of its solubility in ammonium citrate, in which any unchanged tricalcium phosphate, $\text{Ca}_3(\text{PO}_4)_2$ is insoluble, while the monocalcium phosphate has been removed by water. The mono- and dicalcium phosphates together constitute the "available phosphate" in superphosphate and amount to 16 to 18 per cent P_2O_5 .

What is not generally known is that ordinary superphosphate, and indeed other forms of water-soluble inorganic phosphates, are rapidly converted in the soil into forms which are practically insoluble or are only slightly soluble in pure water. The reaction or reversion results in the formation of water-insoluble calcium, iron and aluminum phosphates, and other insoluble phosphates. These compounds are, nevertheless, able to supply sufficient phosphorus to the soil solution for the growth of plants, partly because of their fine state of subdivision. In general, it may be said that inorganic phosphate fertilizers show very little penetration into the soil beyond the zone in which they are applied, except insofar as this zone is disturbed by plowing and other mechanical means.

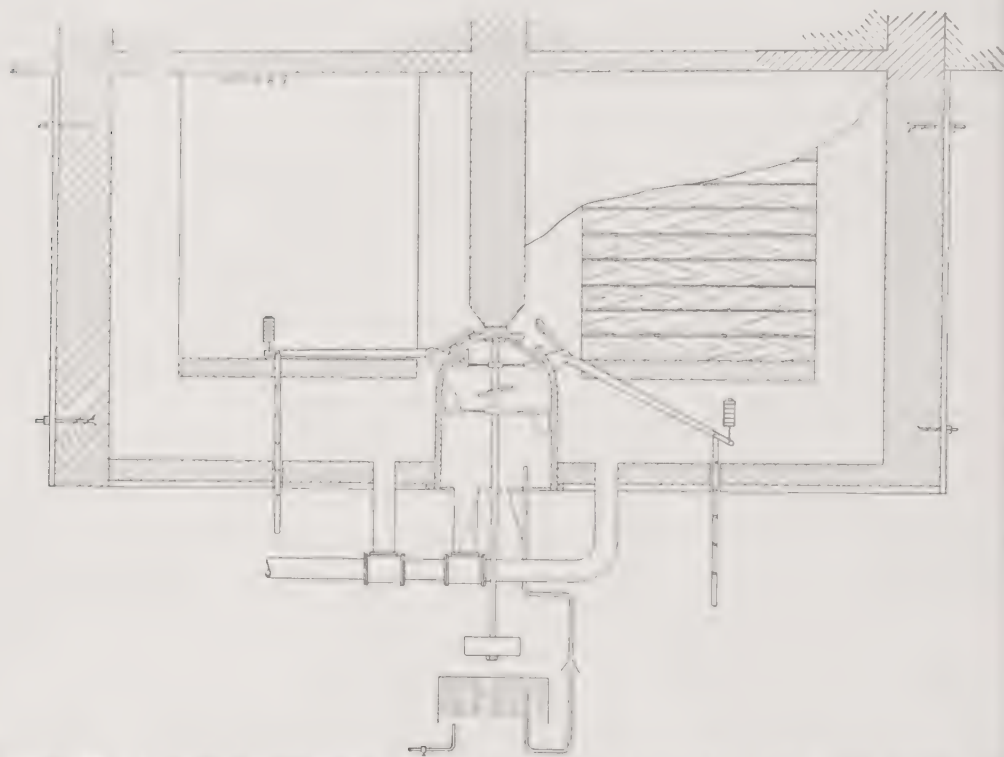


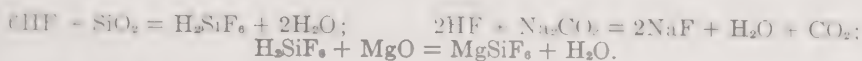
FIGURE 43.—A simple installation for making superphosphate; the mixer serves two pits; outlets for the gases evolved are shown.

To make the superphosphate, the rock is reduced to a powder by means of a jaw-crusher⁶ followed by a continuous pebble mill,⁶ for example. Equal weights of cold acid (first) and powder are run into a cast-iron mixer equipped with paddles, and able to handle 2 tons of rock in each charge. The mass is stirred for 2 minutes, and quickly dumped into the "den" below,

⁶ Chapter 44.

where it remains 24 hours, the reaction started in the mixer continues in the den, and causes a rise in temperature to 100° C. (212° F.). (See Fig. 43.) Carbon dioxide and hydrogen fluoride are evolved, thus making the rock porous. The carbon dioxide comes from a limestone impurity $\text{CaCO}_3 + \text{H}_2\text{SO}_4 = \text{CaSO}_4 + \text{H}_2\text{O} + \text{CO}_2$. The hydrogen fluoride originates in the calcium fluoride present in the rock, $\text{CaF}_2 + \text{H}_2\text{SO}_4 = \text{CaSO}_4 + 2\text{HF}$.⁷

The gases pass out of the mixer and chamber pits under gentle suction, and reach a spray of water in one or more towers. The hydrogen fluoride solution may be neutralized with soda ash, forming sodium fluoride, or it may be treated with more silica (washed sand) to form fluosilicic acid, H_2SiF_6 ; this may in turn be made into sodium or magnesium silicofluoride, the former an insecticide, the latter a preservative for Portland cement surfaces.



After the 24-hour period in the den, the mass is removed by conveyors and bucket elevators to the storage piles, where the superphosphate is allowed to "cure" for 8 to 10 weeks. By curing is meant the further reaction of free acid on unchanged portions of the rock. The longer the period of "cure," the less the amount of acid one needs to apply. In other plants, there is no curing; the mass from the den passes the "rasper," which divides it into uniform, fine grains, and from there to the storage pile, ready for shipment.

The amount of sulfuric acid added is a little less than required for the main reaction (1), in order to avoid residual unchanged phosphoric acid. The water is ample to allow complete wetting of the powdered rock; a part of the excess remains as water of crystallization, $\text{CaH}_4(\text{PO}_4)_2 \cdot \text{H}_2\text{O}$, $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$; some passes out during the period spent in the den. The superphosphate weighs considerably more than the phosphate rock taken (for example, it may be as much as 1.70 times the weight of the 75 per cent tricalcium phosphate rock taken), because the sulfuric acid added remains in the product in the form of gypsum, while most of the water added also remains. There is a loss in fluorine compounds which pass out, but the extra amount of acid which must be added weighs more than the compounds driven out, so that here again there is a gain in weight. By adjusting the amount of acid, its water content, perhaps its temperature, to suit the rock used, a product which is dry, which powders easily, and which does not stick in the drill which applies it to the soil, is obtained.

It has been proposed to produce a dense, granular superphosphate, whose granules would be mechanically strong, and at the same time shorten the manufacturing process from many days to half an hour. This would be done in a horizontal, rotary autoclave.⁸

Triple Superphosphate. A material with three times as much available phosphorus is the triple superphosphate,^{8a} containing 48 to 49 per cent P_2O_5 . It is therefore a far more concentrated product, offering reduced transporta-

⁷ Some of the hydrogen fluoride attacks the silica impurity, forming the gas silicon tetrafluoride SiF_4 , which passes to the towers where it is decomposed by water: $4\text{HF} + \text{SiO}_2 = \text{SiF}_4 + 2\text{H}_2\text{O}$ and later with the cold water, $3\text{SiF}_4 + 2\text{H}_2\text{O} = \text{SiO}_2 + 2\text{H}_2\text{SiF}_6$.

⁸ U. S. Patent reissue 19,825, of original patent 1,947,138.

^{8a} E. L. Larson, *Ind. Eng. Chem.*, 21, 1172 (1929).

tion costs. It is made by the action on phosphate rock of phosphoric acid instead of sulfuric: $\text{Ca}_3(\text{PO}_4)_2 + 4\text{H}_3\text{PO}_4 = 3\text{CaH}_4(\text{PO}_4)_2$. No gypsum is formed, but instead, more of the soluble calcium phosphate. The acid applied contains 45 per cent P_2O_5 , because such strong acid introduces less water which must be evaporated later. The reaction of the rock with phosphoric acid is slower than with sulfuric.

The rock and phosphoric acid are mixed for 1 hour; the resulting solid mass is disintegrated and conveyed to the wet storage building; its moisture content is 20 per cent. After an aging period of 30 days, it is dried at a temperature below 200°C . (392°F .), and ground in a ring-roll grinder to pass a screen with 6 meshes to the inch. It is a stable, nonhygroscopic powder, with 41 to 42 per cent P_2O_5 in the form of water-soluble phosphate, 48 to 49 per cent P_2O_5 as total available phosphate, combined CaO 20.8 per cent, and moisture 2.75 per cent.

Treating ordinary superphosphate with anhydrous ammonia gas permits the fixation of some 3 per cent NH_3 without increasing the consumption of sulfuric or other acid, and gives a product easier to store and apply which, furthermore, does not rot the containing bags.⁹ This has now been extended to treating with urea-ammonia liquor, sodium nitrate-ammonia liquor, and ammonium nitrate-ammonia liquor, with nitrogen content equivalent to 37.5 to 45 per cent nitrogen (compare next chapter).

Soluble Organo-phosphates. Work at the University of Nevada Agricultural Experiment Station during the past several years has been based on the viewpoint that the positional relationships between the plant and the nutrient constitute a factor in the availability of the nutrient to the plant; thus "positional availability," as well as "chemical availability," is important. The ordinary superphosphate already mentioned usually fails to penetrate the soil beyond the depth of plowing or stirring, whereas the root systems of field and orchard crops feed not only in this surface layer but also extensively below that depth. The Nevada experiments have shown several organo-phosphates, such as the phosphoric esters of glycol, glycerol, sorbitol, glucose, etc., and also of ethanol and methanol, to retain their solubility, when in contact with the soil, long enough to permit them to penetrate into the deeper soil layer, and thus supply phosphorus to the deeper portion of the root system. Such penetration by applied phosphate also lessens the possibility of its being lost through erosion of the surface soil. The development of an organo-phosphate of this type cheap enough for practical use has not yet been achieved. The successful solution of this problem promises not only more efficient application of phosphate to the soil, but also would create a large use for cheap or waste organic materials from which a soil-penetrating organo-phosphate could be made.^{9a, 10}

The production of superphosphates in the United States in 1940 was 4,385,971 short tons. (Bureau of the Census.)

⁹ K. D. Jacob, *Ind. Eng. Chem.*, **23**, 14 (1931).

^{9a} Statement kindly prepared by Dr. V. E. Spencer, under date of May 4, 1942, especially for this edition.

¹⁰ "Phosphate Studies: I. Soil penetration of some organic and inorganic phosphates," V. E. Spencer and Robert Stewart, *Soil Science*, **38**, No. 1, 65 (1934); *Proc. Second Dearborn Conference*, (May 1936), p. 37, publ. Chem. Foundation, 654 Madison Avenue, New York. "Organic phosphates: I. Fixation studies with three different soil types," by G. E. Hilbert, L. A. Pinck, M. S. Sherman, and T. H. Trehearne, *Soil Science*, **46**, 409 (1938).

PHOSPHORIC ACID

Wet Method. The major part of the phosphoric acid produced for all purposes is still made by the action of dilute sulfuric acid, 30° Bé., on the ground phosphate rock or bone ash: $\text{Ca}_3(\text{PO}_4)_2 + 3\text{H}_2\text{SO}_4 + 6\text{H}_2\text{O} = 2\text{H}_3\text{PO}_4 + 3(\text{CaSO}_4 \cdot 2\text{H}_2\text{O})$. The calcium sulfate is obtained as gypsum. The reaction may be performed in a lead-lined tank with lead-covered agitator; the calcium phosphate is precipitated, and the clear acid solution containing about 20 per cent P_2O_5 as phosphoric acid is decanted. The mud is washed with water, and the dilute acids obtained concentrated by heat, or used for the dilution of the incoming sulfuric acid from the 50° or 55° Bé. to 30° Bé., ready for treating a new batch. The gypsum may also be filtered in a press, or on sand filters. Improved apparatus has been installed which hastens the separation of the acid from the mud. The Dorr system provides for continuous operation and delivers a first strength of 29 per cent P_2O_5 as phosphoric acid (equivalent to 40 per cent H_3PO_4); a second strength of 15.5 per cent P_2O_5 as acid is employed for the dilution of the chamber or other sulfuric acid. A series of three agitators and six thickeners are used, lined with acid-proof bricks and operated on the counter-current principle; for use in making high-grade fertilizer material, no filtration is required. The mud discharged is free from acid. This artificial gypsum has been utilized for making a number of gypsum products.

When the acid is to be used for baking chemicals, it must be purified from any remaining gypsum, silica, lead, arsenic, iron and aluminum oxides, and fluorine^{10a} compounds. The crude acid is colored green; the purified acid is colorless.

Concentration is performed in lead vessels, by means of lead steam coils, to a 45 per cent P_2O_5 strength, or 50 per cent, at atmospheric pressure. Care is taken to avoid overheating, to prevent the formation of pyrophosphoric acid, $\text{H}_4\text{P}_2\text{O}_7$. Higher strengths than 50 per cent are more readily obtained by the volatilization process.

The yield by the wet method is about 90 per cent over all.

Thermal Methods. Phosphorus and phosphoric acid may be produced without the aid of sulfuric acid, namely, by thermal methods. On heating tricalcium phosphate in the presence of carbon and silica, elemental phosphorus is liberated which, on oxidation and solution in water, gives phosphoric acid. As heating devices, either the electric furnace or the fuel-fired blast furnace may be used. In either case, the reaction which takes place is $\text{Ca}_3(\text{PO}_4)_2 + 5\text{C} + 6\text{SiO}_2 = \text{P}_2 + 5\text{CO} + 3(\text{CaO} \cdot 2\text{SiO}_2)$. The first product is phosphorus; if it is collected under water, and the oxidation performed later as a distinct step, it is the two-pass system; but if air is allowed to join the phosphorus vapor so that it is at once oxidized to P_2O_5 , in the presence of moisture, it is the one-pass system. It should be noted that in the latter, carbon monoxide must also be oxidized, so that the second part of the chemical action is $\text{P}_2 + 5\text{CO} + 5\text{O}_2 = \text{P}_2\text{O}_5 + 5\text{CO}_2$. The solution in water $\text{P}_2\text{O}_5 + 3\text{H}_2\text{O} = 2\text{H}_3\text{PO}_4$ produces the final phosphoric acid.

A flow sheet of the volatilization method, with electricity as the source

^{10a} U. S. Patent 1,858,203 proposes the boiling of the acid with hydrated silica such as diatomaceous earth, followed by the addition of soda ash and decantation from the sodium fluosilicate produced.

of heat, illustrates the one-pass process. (See Fig. 44.) The rock or pebbles, crushed to small size, is mixed with sand and coke, and fed to an electric furnace having 3 electrodes. The furnace consists of a cylindrical steel shell lined with fire-bricks; the cover has an outlet for the gases which pass through a wet dust catcher to a Cottrell precipitator wherein the phosphoric acid mist is precipitated. The calcium silicate slag passes out of the furnace at the tap hole; given the proper impurities or additions, the slag may be a valuable cement. The flow sheet includes a scheme for making ammonium phosphate.

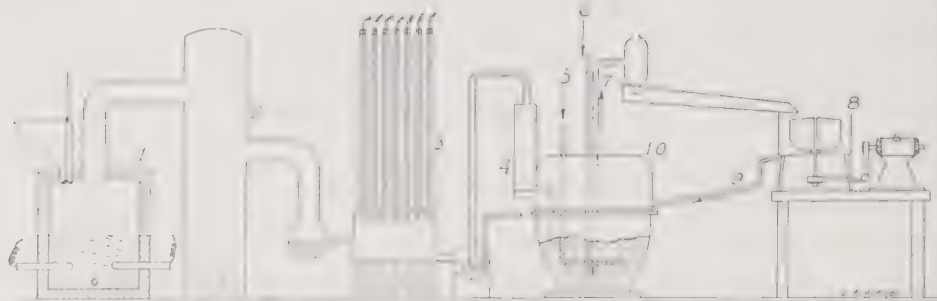


FIGURE 44.—The volatilization process for phosphoric acid, and saturator for ammonium phosphate manufacture; 1, furnace; 2, dust catcher; 3, electrical precipitator; 4, entry of phosphoric acid liquid into saturator; 5, ammonia gas inlet with distributor; 6, compressed air line for continuous ejection of suspension of crystals through 7 to centrifugal 8, with run-back 9 for the clear liquor.

In the development¹⁰⁵ of the Tennessee Valley Authority, (T. V. A.) there has been included a fertilizer plant, in which superphosphates are produced. An electric furnace, using about 4,800 kwh. per ton of P_2O_5 charged, sends its gases, phosphorus and carbon monoxide, (a) to be oxidized together, wasting the carbon monoxide, and giving phosphorus pentoxide which is then hydrated to the acid; or (b) to a cooler where the phosphorus is condensed as a liquid under water, allowing the carbon monoxide to be burned usefully by itself. The phosphorus is then oxidized and hydrated later. The absorption of the P_2O_5 in 85 per cent phosphoric acid runs smoothly and is full of promise.

The temperature at which reduction takes place is 1300° to 1400°C . (2372° to 2552°F.); 40 per cent of the total heat supplied raises the charge to 1300°C . (2372°F.); the 60 per cent which causes the reduction must be supplied above 1300°C . This the electric furnace does well. On the other hand, the extremely high heat of the arc may volatilize lime, silica, alumina, magnesia; a number of ingenious dispositions and inventions have been necessary in order to prevent this difficulty.

In the blast furnace, 2.36 pounds of coke are consumed for each pound of phosphorus pentoxide, P_2O_5 , produced. The yield for the thermal method is 80 per cent; phosphorus is lost to iron and other impurities left in the furnace.

Phosphorus pentoxide is a white powder, extremely hygroscopic. Phosphorus is a yellow, wax-like solid, which melts at 44°C . (111.2°F.); it is

¹⁰⁵ "The manufacture of phosphoric acid by the electric furnace method," Harry A. Curtis, *Trans. Am. Inst. Chem. Eng.*, 31, 278 (1935) with illustrations, flow sheet (p. 282), and diagrams.

under water, for in the air it oxidizes spontaneously to its white powdery oxide.

The thermal methods have the advantage of permitting the manufacture of any strength phosphoric acid desired; the higher strengths are obtained without the necessity of concentrating by heat. The acid produced is, furthermore, much purer.

Trisodium Phosphate. Trisodium phosphate, $\text{Na}_3\text{PO}_4 \cdot 12\text{H}_2\text{O}$, is an alkaline substance which has come to be highly prized as a detergent, a water-softener, and boiler compound. It is made in two steps. First, phosphoric acid is neutralized with soda, with the formation of disodium phosphate: $\text{H}_3\text{PO}_4 + \text{Na}_2\text{CO}_3 = \text{Na}_2\text{HPO}_4 + \text{CO}_2 + \text{H}_2\text{O}$. The third hydrogen atom in phosphoric acid is unaffected by soda ash. To the solution of the disodium phosphate, caustic soda is added, with the formation of the trisodium salt: $\text{Na}_2\text{HPO}_4 + \text{NaOH} = \text{Na}_3\text{PO}_4 + \text{H}_2\text{O}$.

In a 4000-gallon tank with agitator, 7000 pounds of soda ash are suspended in 900 gallons of hot water or hot wash liquor; phosphoric acid of 45 per cent P_2O_5 content in the proper amount is added at the surface, so that the carbon dioxide evolved may escape more readily.¹¹ The solution is boiled to remove all carbonate, diluted with mother liquor from previous crystallizations, and filter-pressed hot. In the next step, 1500 gallons of disodium phosphate solution (14.5 per cent P_2O_5 and 13 per cent Na_2O) are treated with some 2800 pounds of sodium hydroxide dissolved in 300 gallons of hot water, and then 1000 gallons more of the disodium liquor of the same strength. The resulting solution is diluted with mother liquor from the crystallizer to a specific gravity of 1.34 to 1.40 at 90° C. (194° F.). It is filter-pressed, and delivered through steam-jacketed pipes to water-cooled crystallizers; the liquor fed in has a temperature of 70° C. (158° F.) and contains 9.25 per cent P_2O_5 and 13.2 per cent Na_2O . The temperature is reduced gradually to 30° C. (86° F.). The crystals formed are centrifuged, dried in a jacketed rotary drier, cooled, and screened.

A spray-congealed grade is made by adjusting the concentration to match that of $\text{Na}_3\text{PO}_4 \cdot 12\text{H}_2\text{O}$, and atomizing at the top of a tower; during the free drop of 70 feet, the particles assume a spherical shape and congeal. The product is screened. To reduce caking, a small amount of another salt (NaF , NaCl) may be added.

The preparation of disodium phosphate has been given incidental to the manufacture of trisodium phosphate, at least as far as its solution. In order to obtain the salt, this solution is crystallized, the crystals centrifuged and packed. Disodium phosphate is $\text{Na}_2\text{HPO}_4 \cdot 12\text{H}_2\text{O}$ and effloresces (loses water of crystallization) in the air. It is a valuable agent for water softening. The monosodium salt is also made, but in smaller quantities; this is an acid substance, and serves among other things as a baking chemical. By heating the monosodium phosphate NaH_2PO_4 , sodium acid pyrophosphate, with better keeping qualities, is obtained: $2\text{NaH}_2\text{PO}_4 + \text{heat} = \text{Na}_2\text{H}_2\text{P}_2\text{O}_7 + \text{H}_2\text{O}$.

The production* for the sodium phosphates in 1939 was:

¹¹ Trisodium phosphate, its manufacture and use." Foster D. Snell, *Ind. Eng. Chem.*, 23, 470 (1931).

* Bureau of the Census.

	Tons	Price per ton
Trisodium phosphate	114,687	\$ 42.00
Disodium phosphate	13,627	90.60
Monosodium phosphate	3,197	136.20
Sodium pyrophosphate	42,210	99.60
Sodium metaphosphate, ammonium phosphate, and others, value \$4,394,627.		

Monocalcium Phosphate. Monocalcium phosphate is manufactured in considerable quantities, chiefly as a baking chemical. It is made from purified phosphoric acid, by the addition of selected hydrated lime or limestone: $2\text{H}_3\text{PO}_4 + \text{CaCO}_3 = \text{CaH}_4(\text{PO}_4)_2 \cdot \text{H}_2\text{O} + \text{CO}_2$. After mixing, the materials are set aside to allow the reaction to become complete; the result is a solid, which is crushed to a medium size. It is then dried at a gentle heat, which causes the loss of the water of crystallization. The product is milled to the desired granulation, and packaged; it is practically pure monocalcium phosphate.

Dicalcium phosphate is obtained as a by-product in the manufacture of ossein; see Chapter 36.

Ammonium phosphate has the advantage of supplying two of the necessary elements for plant food in a single substance. Monoammonium phosphate is made by passing ammonia into strong, hot phosphoric acid until the composition corresponding to $\text{NH}_4\text{H}_2\text{PO}_4$ has been reached; on cooling a rich crop of crystals forms; these are centrifuged and dried to a stable, white powder, having the formula $\text{NH}_4\text{H}_2\text{PO}_4$. The flow sheet for phosphoric acid by volatilization illustrates the preparation of this salt.

The *diammonium phosphate*, containing some of the mono salt, is more difficult to prepare. Both are made in increasing quantities, with synthetic ammonia. In the crop year 1940-41, 48,000 tons of ammonium phosphate (Ammophos) were produced and used in making fertilizers. (U. S.)

Consumption statistics on phosphoric acid and its compounds are given in Table 15.

TABLE 15.—Annual consumption of P_2O_5 in form of phosphoric acid, phosphate salts and triple superphosphate (but not ordinary superphosphate), all phosphoric acid products.*

	Tons
Phosphoric acid, all grades	6,500
Monocalcium phosphate	21,500
Ammonium phosphates	3,700
Disodium phosphate	14,500
Trisodium phosphate	15,600
Sodium acid pyrophosphate	1,100
Triple superphosphate (for fertilizers)	18,000
Total	80,900

The figure for the triple superphosphate is only for the phosphoric acid consumed as such in making 60,000 tons of triple superphosphate (at 45 per cent P_2O_5).

* William H. Waggaman, *Ind. Eng. Chem.*, 24, 984 (1932).

BAKING POWDERS

Baked food products owe their light structure to the presence of carbon dioxide evolved within the dough during its preparation and the early stages of baking. The carbon dioxide may be produced by yeast (bread) or by baking powders (cakes); the latter generate the gas more rapidly, partly at once on being mixed and moistened, the rest on application of heat.

baking powder, then, is a combination of chemicals, called the baking chemicals, which yield the carbon dioxide gas on being moistened. The amount of gas is calculated to be 14 per cent (by weight) for household powders and 17 per cent for commercial powders. The standardization is performed by selecting the materials stronger than necessary, and diluting

FIGURE 45.—Mixers and weighing hoppers for ingredients for baking powders. The mixers contain 5000 lbs. of baking powder. Note that the mixer is on wheels and may be moved to any one of the bins. (Courtesy of the Rumford Chemical Works, Providence, R. I.)



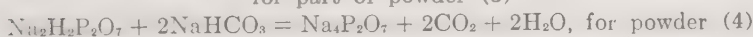
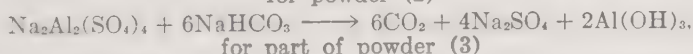
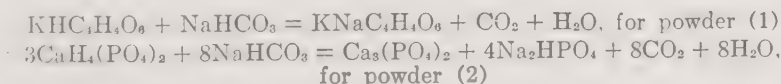
them to the right strength by the addition of cornstarch. After gas evolution, the residual chemicals must be without harmful action on the human system. Figure 45 shows the equipment for mixing and weighing the ingredients.

Three types of baking powders are estimated to constitute 90 per cent of all the baking powders produced (U. S.); their quantitative formulas to yield 14 per cent CO_2 are as follows:

	Cream of tartar	Calcium acid phosphate Per cent	S.A.S. phosphate
Sodium bicarbonate	26.73	26.73	26.73
Cornstarch	22.40 (1)	39.84 (2)	40.07 (3)
Tartaric acid	5.97
Cream of tartar	44.90
Monocalcium phosphate	33.43	13.28
Sodium aluminum sulfate (calcined).....	19.92

In addition to these three, a fourth type (4) is sold to commercial bakers, often in the form of the separate unmixed ingredients; when made up, it contains 30.59 per cent sodium bicarbonate, 29.03 per cent cornstarch, and 40.38 per cent sodium acid pyrophosphate, $\text{Na}_2\text{H}_2\text{P}_2\text{O}_7$. This powder evolves 17 per cent gas.

It will be noted that all baking powders have the same carbon-dioxide-generating chemical, NaHCO_3 , and differ only in the acidic substance. The reactions are probably as follows:



The manufacture of the baking chemicals has been described in the preceding chapters, except for cream of tartar, $\text{KHC}_4\text{H}_4\text{O}_6$, and tartaric acid, $\text{H}_2\text{C}_4\text{H}_4\text{O}_6$. Both are solids, and by-products of the fermentation of wine during which a deposit forms, called argol. It is collected, dissolved, filtered, pressed, decolorized by passing through bone char, and the clear liquid crystallized in shallow vats. The product, after drying and powdering, is pure cream of tartar, $\text{KHC}_4\text{H}_4\text{O}_6$.

Wine lees contain, besides the potassium salt, much of the calcium salt. By treating with sulfuric acid, the calcium is precipitated as sulfate, and the mother liquor may be crystallized to give tartaric acid $\text{H}_2\text{C}_4\text{H}_4\text{O}_6$, or, written out to show its structure, $\text{HOOC} \cdot (\text{OH})\text{HC} \cdot \text{CH}(\text{OH}) \cdot \text{COOH}$. This tartaric acid and the tartrates described are exclusively the dextro-rotatory isomers.¹²

Cornstarch is presented in Chapter 23.

The production of baking powders of all kinds for the year 1939 was 140,230,992 pounds, valued at 9.8 cents a pound; yeast and other leavening compounds for the same year amounted to 219,364,386 pounds, valued at 7.7 cents a pound.

OTHER PATENTS

U. S. Patents: 1,688,112, on trisodium phosphate and its manufacture; 1,633,213, on the use of trisodium phosphate in cleaning, whitening, filling and weighting fabrics; 1,758,448-9, on ammonium phosphate by leaching raw phosphate with an acid; 1,878,911, manufacture of phosphates and phosphoric acid using H_2SO_4 ; 1,845,876, alumina and alkali phosphates by decomposition with caustic alkali; 1,822,040, diammonium phosphate; 1,831,653, leaching phosphate rock with HNO_3 ; 1,837,284, producing soluble phosphate using SO_2 and nitrogen oxides; 1,753,478, dicalcium phosphate used as by-product HCl on phosphate rock; 2,055,332, purification of sodium metaphosphate; 2,062,866, making sodium phosphate; 2,069,182, the application of sulfonated oil to the mineral concentration for Florida phosphate debris; 1,991,916, method and apparatus for oxidizing phosphorus; 1,988,387, production of phosphorus; 1,869,941, 1,837,321, 1,947,138, reissue 19,825, a rapid method for manufacturing superphosphate.

PROBLEMS

1. Seven tons of phosphate rock containing 76 per cent tricalcium phosphate and acidulated with 50° Bé. sulfuric acid (62.18 per cent H_2SO_4), in order to prepare ordinary superphosphate. Taking just the right amount of acid for the reaction with the phosphate, how many pounds will be required? Leaving the reactions with calcium fluoride and calcium carbonate out of account, and assuming that there remains moisture content of 2.3 per cent, what will be the weight of the produced superphosphate? The new compounds formed are $\text{CaH}_2(\text{PO}_4)_2 \cdot \text{H}_2\text{O}$ and $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$.

2. What is the percentage of P_2O_5 in the rock described in Problem 1? Making the assumption again that the reaction runs as the theory requires, what is the percentage of P_2O_5 present as water-soluble phosphate in the finished product? What would it be, if you started with 100 per cent tricalcium phosphate?

3. A shipment of 87 tons of Florida land pebble phosphate contains 34.96 per cent P_2O_5 in the form of tricalcium phosphate, and 3.92 per cent F in the form of calcium fluoride. The limestone impurity is 7.7 per cent, and the remainder is clay, silica and moisture. What is the composition of the rock, as far as this information indicates it? What is the exact amount of 50° Bé. sulfuric acid which will be required, all reactions proceeding as required by the theory? How much gypsum will be formed in all? Let all the fluorine escape as HF , how much hydrofluoric acid in the form of 60 per cent acid will be collectable, in pounds? What is the weight of carbon dioxide evolved, and how much will be the final product weight, moisture to be again 2.3 per cent?

4. Sulfuric acid of 30° Bé. strength (34.63 per cent H_2SO_4) is to be used for making 9 tons of 40 per cent phosphoric acid (H_3PO_4), equivalent to a 29 per cent P_2O_5 content.

¹² The unraveling of the various forms of tartaric acid was the first achievement of Louis Pasteur in 1852.

1254 sp. gr.). A low-grade calcined rock with 27.6 per cent P_2O_5 content is used. How much sulfuric acid will be required, and how much rock? How much sodium phosphate will be obtained? The yield must be taken as 88 per cent.

5. A shaft furnace produces 47 tons of 85 per cent phosphoric acid (H_2PO_4) per day. The rock required is 2.56 pounds per pound of P_2O_5 produced. How much rock is required per day? The yield is 80 per cent over all; how much 75 per cent trisodium phosphate rock will be needed? If all the phosphorus pentoxide produced in the yield was first collected as yellow phosphorus, how many pounds were there?

6. The 7000 pounds of soda ash under trisodium phosphate (see text) are made into disodium phosphate, without additions. How many pounds are obtained in solution, and how many pounds of 45 per cent P_2O_5 phosphoric acid were required; how many pounds of 98.6 per cent NaOH must be added to form the trisodium phosphate, assuming perfect recovery? If the product crystallizes with $12H_2O$, how many pounds are obtained, and what is the percentage of sodium phosphate in the crystals?

7. One-half ounce of baking powder of Formula (2) will generate what weight of CO_2 , and what volume will the gas have at room temperature?

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The knowledge of the requirements of vegetation rests on chemistry; on this knowledge in turn rests the choice of fertilizing agents. considerable part of the fertilizers used are produced, or at least modified by industrial chemical operations. With the aid of commercial fertilizers the productivity of a given area may be raised, and a greater number of people may be supported by its yield.

Chapter 8

Fertilizers, Mixed Fertilizers, Potassium Salts, Natural Organic Fertilizers, Synthetic Urea

The greater part of the food supply of the human race comes from the soil, in the form of vegetables and grains, or of meat from domestic animals fed on the products of the cultivated soil. Plants need the following substances for their growth: water, nitrogen compounds, phosphorus compounds, and potassium compounds, in fair quantities; lime, iron, magnesium and sulfur compounds in small quantities. The observation that soils become exhausted by successive crops was made many centuries ago. In order to prevent this exhaustion the ancients allowed a field to "fallow" every third season. During that period the particles of rock in the soil weathered and became soluble, furnishing an extra amount of plant food which was ready for use in the succeeding season. Potassium from the felspar and, to a lesser extent, phosphates from the phosphate rocks, were thus accumulated in the soil; the same process goes on to-day. The ancients also knew the use of manure and the fact that to plant certain grasses and plow them into the soil enriched it. Manure is still used to-day, and crops of clover are grown and plowed under in order to enrich the soil with nitrogen compounds. Wood ashes were used, and supplied, as is now known, potassium carbonate. Thus the merit of modern fertilizing science is not that it has discovered the process, but rather that it has explained it. The particular elements furnished by manure, wood ashes, and clover are known and supplies of the necessary plant foods are furnished by mines and factories in almost limitless quantities.

In stable manure, the nitrogen compounds are chiefly urea, $\text{NH}_2\text{CO.NH}_2$ and ammonium salts; at the same time manure supplies organic materials which form the "humus" which every fertile soil contains. Manure is a by-product of the farm and need not be purchased; hence its general use. It is supplemented by nitrogenous compounds from various sources, such as ammonium sulfate from ammonia recovered during the distillation of coal or made from synthetic ammonia; synthetic urea; sodium nitrate from Chile or synthetic; calcium and other nitrates made by nitric acid resulting from the oxidation of synthetic ammonia; calcium cyanamide. The manufacture or method of extraction of these substances is discussed under the appropriate headings. Other important sources of nitrogen in suitable compound form are dried blood (13 per cent N), tankage (from garbage), sewage disposal sludge, bone meal, dried albumen, dried fish scraps, oil meal such as

pressed cottonseed meal which for one reason or another cannot be used as cattle food, and a number of other materials of animal origin.

Phosphorus is applied in various forms. Finely powdered phosphate rock is applied directly,¹ to the extent, for example, of 50,000 tons in 1924; it is insoluble in water, but weathers fast. Superphosphate with 16 to 18 per cent P_2O_5 is used to a far greater extent; its phosphate is soluble, and therefore of immediate service to the plant. Triple superphosphate, with 48 per cent P_2O_5 , is gradually coming into use.

The effect of fluorine on the efficacy of phosphate materials has been studied.*

The slag from the Thomas and Gilchrist process² contains calcium phosphate, which is insoluble in water, but which weathers more readily than the tricalcium phosphate in phosphate rock; it is applied directly to the soil, after powdering. The content of iron is high (7 to 10 per cent in oxides), but does not interfere with the fertilizing properties. The slag is very hard and must be powdered in a special ball mill with hard steel balls. Slag phosphate is of no importance in the United States, but it is used in Europe.

Precipitated tricalcium phosphate is absorbed by the plant more rapidly than the rock phosphate; a very finely divided tricalcium salt is the "colloidal phosphate" from Florida.¹ Another important material supplying phosphorus is bone meal.

Potassium salts, chiefly the chloride, are obtained from deposits in the earth, from brine ponds in arid regions, and other sources, as fully discussed in this chapter; they are sold in various grades or strengths, reported on the basis of potassium oxide K_2O , a convenient way to rate them.

Mixed fertilizers contain nitrogen as nitrates, urea, ammonium salts, or other nitrogen-containing compounds; phosphorus as superphosphate and potassium salts, chloride or sulfate; the order given above is the one generally used, so that a 2-8-2 fertilizer would contain 2 per cent nitrogen, 8 per cent phosphoric acid anhydride (P_2O_5), and 2 per cent potassium oxide, K_2O . The formulas differ for the several crops: for late potatoes, 4-8-10; wheat, 2-12-6; sugar beets, 4-12-6; clover, 0-12-15; strawberries, 5-8-7. This method of evaluation in terms of nitrogen, phosphoric acid, and potassium oxide is merely for convenience; the compounds actually present are those given above. Sodium nitrate (Chilean) may be mixed with superphosphate, or applied by itself. The mixed fertilizer usually contains some inert material, such as earth or gypsum; its function is mainly to dilute, but also to act as a drier, preventing the caking of the powder.

The mixing of "complete" fertilizers is done in a revolving mixer, unlike a cement mixer, or in any other type mixer if found suitable; the several ingredients are dumped (horse-drawn cart) into a hopper; a bucket elevator feeds the mixer. The batches are of several tons each.

The complete fertilizers refer to nitrogen, phosphoric acid (as P_2O_5) and potassium oxide; but although these three elements are the most important

¹ K. D. Jacob, *Ind. Eng. Chem.*, 23, 15 (1931); see also Chapter 7.

* "Fluorine, its effect on plant growth and its relation to the availability to plants of phosphorus in phosphate rocks," by R. P. Bartholomew, Arkansas Agric. Exp. Station, *Soil Science*, 40, 203 (1931).

² Chapter 48.

It might be mentioned that eleven elements are required for successful growth of plants: phosphorus, nitrogen, potassium, calcium, sulfur, magnesium, iron, boron, carbon (in large part from the atmosphere), hydrogen, and oxygen.

The fertilizing values may be concentrated by manufacturing, for example, ammonium phosphate, which would contain both nitrogen and phosphoric acid, or potassium nitrate, containing potassium and nitrogen. For long shipment, high concentrations are desirable, since the freight on inert matter is saved. The wider use of concentrated fertilizers promises to be the next great development in this field.

Ammoniated Superphosphates. There has come into prominence of late the method of spraying a very strong ammonia, as for example anhydrous ammonia with 40 to 80 per cent NH_3 , onto a charge of superphosphate contained in a revolving mixer, so that new surfaces are continually exposed. The relation may be 5 parts of NH_3 to each 100 parts of superphosphate (18 per cent P_2O_5). The ammoniated superphosphate has an increased value; also any residual sulfuric acid is neutralized, and the "rotting" of the bags from that cause is avoided. A mixed fertilizer may also be ammoniated by means of very concentrated hydrous ammonia, delivered from a steel pressure tank similar to the anhydrous ammonia containers. For example: superphosphate 900 pounds, sulfate of ammonia 52 pounds, manure salts 267 pounds, filler (sand) 673 pounds, total 1892 pounds, may be treated with 108 pounds of NH_3 in the form of 40 to 80 per cent hydrous ammonia. The anhydrous material is rarely used, for a certain quantity of water seems to be necessary to produce the essential grain structure, and avoid the undesirable powder structure which anhydrous ammonia brings about.^{2a} This new development is a result of the decreased price of ammonia, from the 25 cent level of 15 years ago to below 6 cents a pound.

As a logical extension of this practice a urea-containing ammonia liquor has been on the market since 1932 and has found increasing favor; it contains 15.1 per cent nitrogen in the form of urea, and 30.4 per cent as ammonia (NH_3), with a total of 45.5 per cent nitrogen. Rivaling this is the sodium nitrate-containing ammonia liquor with a total nitrogen content of 44.4 per cent, and ammonium nitrate in ammonia liquor, with a total of 37.5 per cent.^{2b} About 180 pounds of the urea-ammonia liquor and 400 pounds of the ammonium nitrate-ammonia liquor can be added to a ton of superphosphate without causing reversion.

The ammoniation of superphosphates in this way has been a distinct advance in the science of fertilizer manufacture.

Sodium Nitrate Solid Pellets. It has been found advisable to alter the condition of Chilean nitrate intended for fertilizer mixing, by forming it into round pellets, in order to remove its hygroscopic property. The method^{2c} consists of melting the nitrate at the temperature of not over 350° C. [662° F.], forcing it through a filtering screen, and spraying it

^{2a} U. S. Patent 2,060,310.

^{2b} Compare p. 57, report 114, U. S. Tariff Commission, described under reading references; also booklets "Urea-ammonia Liquor-A" (1933) and "UAL-B," (1936) Du Pont Company, Ammonia Department, Wilmington, Del.

^{2c} U. S. Patent 1,937,757.

into a cooling chamber; there results a product consisting of small balls with a hard outer surface, and solid throughout. Another method^{2d} provides for the incorporation of 5 per cent potassium nitrate, magnesium nitrate or ammonium sulfate, giving again a non-hygroscopic, solid, hard pellet, well suited to the agricultural drill which applies the mixed fertilizer to the soil. This improvement has been carried over into synthetic nitrate manufacture.

POTASSIUM SALTS

The most extensive mineral deposits of soluble potassium salts are those at Stassfurt, in Germany, which supplied nearly all the world's requirements until 1914. Since the end of the first World War, the deposits in upper Alsace, near Mulhouse, have been developed until they yield about one-third of the Stassfurt tonnage; they are similar in nature to the German deposits. A third deposit of similar character lies in Poland, near Kalusz in the southeastern part, and yielded 261,310 tons of potassium salts of all grades in 1931. The German production was about $1\frac{1}{2}$ million tons for that year. A fourth producing deposit is the one in Carlsbad, New Mexico, which began shipments in 1931.

The Stassfurt area lies in the central part of Germany, between Magdeburg and Halle. The deposits of the potash beds are at a depth of about 1000 feet, and overlie a bed of salt (NaCl) 3000 feet thick. Over the potash beds a layer of clay separates them from another deposit of salt (NaCl) of more recent geological origin. Three potash layers are distinguished, of which the upper is 300 feet thick and extends over many square miles; it consists of carnallite, $\text{MgCl}_2 \cdot \text{KCl} \cdot 6\text{H}_2\text{O}$ (40%), mixed with salt (20%) and other impurities. Below the carnallite lies polyhalite, $2\text{CaSO}_4 \cdot \text{MgSO}_4 \cdot \text{K}_2\text{SO}_4 \cdot 2\text{H}_2\text{O}$, and below this, kainite, $\text{MgSO}_4 \cdot \text{KCl} \cdot 3\text{H}_2\text{O}$. The geological history of these deposits is that salt deposited from sea water leaving a mother liquor which gradually gained in potassium salt content; a change in the topography caused the isolation of the bay, and the lake so formed dried completely; it was during this dry period that the potassium salts deposited. A similar relation of solubilities is exhibited by present-day sea water, which is evaporated for salt in the south of France: after the salt has deposited, the more soluble magnesium salts with some potassium remain in the mother liquor, and are run off because the magnesium is bitter.

The method of mining at Stassfurt is by shafts and tunnels. The mineral is dislodged by blasting with black powder; it is loaded in mine cars and hauled to the refining plant at the mouth of the shaft.

The German potash salts for fertilizer purposes are produced in four grades. Their value is based largely on the calculated potassium oxide equivalent: kainite, with 12 per cent K_2O ; manure salts, with 20 per cent potassium chloride, with 50 per cent; potassium sulfate, also with 50 per cent.

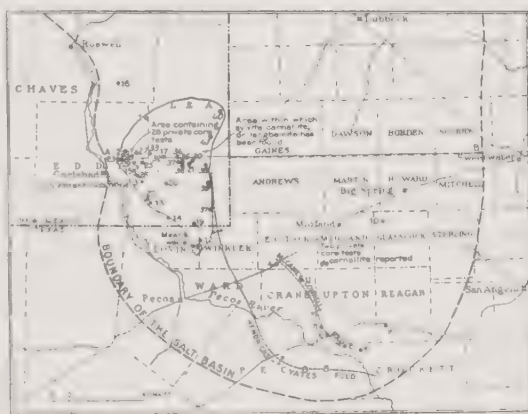
The crude carnallite is refined to potassium chloride by treating the crushed material with a hot solution of 20 per cent magnesium chloride from a previous operation. In this solution, the salt (NaCl) is insoluble

and is left behind with calcium sulfate and other impurities; from this solution, potassium chloride deposits on cooling. The mother liquor is concentrated and gives on cooling a lower grade of potassium chloride utilized as manure salts. The first crop of potassium chloride may be refined further by washing with cold water; this further treatment is applied only to a limited quantity.³

The Alsatian deposits⁴ consist of two strata. The upper one is about 3 feet thick, and contains 35 to 40 per cent potassium chloride; the depth is 1500 feet below the surface in one section, but greater in others. The lower layer is 7.5 to 16 feet in thickness, and lies about 50 feet lower; it contains 24 to 32 per cent potassium chloride. Both layers are essentially sylvinite, $\text{KCl} \cdot \text{NaCl}$, containing sodium chloride as impurity, and clay; the purification is by crystallization, and leads to potassium chloride 98 per cent pure (or with 61 per cent K_2O content). Lower grades are obtained from mother liquors; a part of the mine product is shipped after mere crushing. The grades marketed are: sylvinite, 12 to 16 per cent K_2O ; sylvinite rich, 20 to 22 per cent or 30 to 32 per cent; potassium salt (*scl de potasse*), 40 to 42 per cent; and potassium chloride (*chlorure de potasse*), 62 per cent K_2O . The first two are crushed mineral; the last two have been concentrated by solution and crystallization.

The American deposits lie in the southeastern part of New Mexico, in Eddy and Lea counties, and in the neighboring counties in Texas, Loving, Winkler, Ector, Crane, Upton, Reagan and Crockett. (See Fig. 46.) The

FIGURE 46.—Map of the Permian potash field in Texas and New Mexico. (Courtesy of the Department of the Interior, U. S. Geological Survey.) The dots and numerals mark test drilling locations.



deposits are of Permian age. The area covers underground deposits of rich potassium salts, chiefly chloride; in Eddy County, there are ten beds at depths between 800 and 1762 feet below the surface, varying in thickness from 1 foot 2 inches to 4 feet 6 inches, and having an arithmetical total of 36 feet. (See Fig. 47.) The potassium minerals are sylvinite (the richest), kainite, and some polyhalite. At a depth of 1267 feet, the bed is 3 feet 6 inches of sylvinite; at 1311 feet another deposit of 3 feet occurs, consisting of sylvinite and polyhalite; while at 1365 feet depth, a 2-foot

³ To the north and northwest of the Stassfurt basin potassium salts are also found, in Hannover, Brunswick, and Mecklenburg; these deposits are smaller, and consist chiefly of sylvine or sylvinite, $\text{KCl} \cdot \text{NaCl}$, more or less pure.

⁴ "The Alsatian potash industry," Henri Vigneron, *Chem. Met. Eng.*, 24, 655 (1921), with 16 illustrations.

thick bed of sylvinite is available. A shaft sunk near Carlsbad, New Mexico, serves a mine operating since 1931; in that year, a large tonnage was produced, with a content of 25.6 per cent K_2O . The mineral was higher in potash than the test cores had indicated.

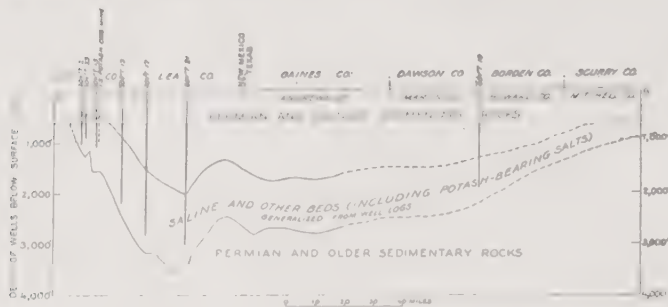


FIGURE 47. — Projected section of Permian potash field in Texas and New Mexico. (Department of the Interior, U. S. Geological Survey.)

In addition, there are numerous beds of polyhalite, an impure potassium sulfate, averaging close to 10 per cent K_2O , at depths of 1100 to 2752 feet under the surface.⁵ The thickest bed is 15 feet 6 inches, at a depth of 1459 feet, with 8.8 per cent K_2O , in Eddy County. The deepest down is in Winkler County, Texas, where at 2267 feet depth, a bed of 9 feet 8 inches occurs, with 7.23 per cent K_2O , and just over it, at 2257 feet depth, a layer 6 feet thick is found, with 10.63 per cent K_2O . The richer minerals tapped by the Carlsbad shaft has not been found in the Texas counties.

A refinery has been erected at Carlsbad, N. M. (Potash Company of America) in which a flotation method is used for the separation of potassium chloride from its valueless companion in sylvinite, sodium chloride. The production is near 100,000 tons of KCl , with 60 per cent K_2O .

The New Mexico and Texas deposits were probed during and since the war of 1914-18, by private citizens and by government agencies. The Mulhouse deposits are due solely to private enterprise; they were discovered while searching for petroleum, before 1914.

Potassium Salts from Brines. Besides the important mineral deposits of Stassfurt, Alsace, southeastern Poland, New Mexico and Texas, brines from lakes in dry areas furnish potassium salts. Of the numerous enterprises begun within the U. S. during the war of 1914-18 to relieve the shortage due to the blockade of German seaports, only one survived, that of the American Trona Company at Searles Lake,⁶ in the dry desert between

⁵ Regarding the possible exploitation of the polyhalite beds, it might be noted that potassium in the form of the sulfate is the preferred form for the fertilization of the citrus fruit crop. H. H. Storch, *Ind. Eng. Chem.*, 22, 934 (1930); Everett P. Partridge, *Ind. Eng. Chem.*, 24, 896 (1932).

⁶ Searles Lake.

Composition of Searles Lake Brine.

	Per cent by weight
$NaCl$	16.35
Na_2SO_4	6.96
KCl	4.75
Na_2CO_3	4.74
* $Na_2B_4O_7$	1.51
† Na_3PO_4	0.155
$NaBr$	0.109
Miscellaneous	0.076
Total Solids	34.65
Water by diff.	65.35

* Equiv. to 2.86 per cent $Na_2B_4O_7 \cdot 10H_2O$.

† Equiv. to 0.067 per cent P_2O_5 .

The American Potash and Chemical Corporation uses vacuum crystallization extensively, (see Perry "Chemical Engineers Handbook," p. 1486), saving space, circulating water, and material in process.

California and Nevada. This lake is really a deposit of solid salts with a brine permeating them; the salts are stiff enough to carry a dirt road. The brine is pumped to the plant, concentrated in triple-effect evaporators 50 feet high, in which common salt precipitates; the concentrated liquor on cooling deposits crude potassium chloride, which is refined to contain 60 per cent KCl . Borax is produced from the same brine, by agitating it, after the potassium salts have deposited in the quiet liquor. The output per year is about 50,000 tons of high-grade potassium chloride. Up to a few years ago, the bulk of the world's borax was produced from colemanite, $\text{Ca}_2\text{B}_6\text{O}_{11} \cdot 5\text{H}_2\text{O}$, by decomposing with boiling sodium carbonate, filtering and crystallizing. Development of Searles Lake brine with its additional products of potassium chloride and sodium sulfate made it possible to produce borax more cheaply than from colemanite. However, at about the same time, extensive deposits of rasorite, $\text{Na}_2\text{B}_4\text{O}_7 \cdot 4\text{H}_2\text{O}$, were discovered near Kramer, California, which are now mined, the ore shipped to Los Angeles Harbor, dissolved in water under heat and pressure, strained, filtered and crystallized as pure borax, $\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$.^{6a}

The production of crude borates from all sources was 243,355 tons, valued at \$23.10 a ton (U. S. 1940).

A similar brine from a drying salt lake near Zarzis in Tunis is the basis of a growing industry.⁷ The exploitation of the brine in the Dead Sea is now under way. The production is to be at the rate of 1000 tons annually for nine years, then 50,000 annually for the next ten years. The relative sizes of the sources already discussed may be indicated by the reserves, figures for which are as follows: Stassfurt, 8 billion tons K_2O ; Mulhouse basin, 350 million; Dead Sea, 2 billion, and Searles Lake, 20 million.

There are other mineral sources of potassium. Alumite, $\text{K}_2\text{Al}_6(\text{OH})_{12}(\text{SO}_4)_4$, is mined and worked for potassium sulfate in Sulphur, Nevada, and Marysville, Utah. On roasting, the aluminum sulfate is decomposed, and the potassium sulfate may be leached out.⁸ Leucite, $(\text{KNa})\text{AlSi}_2\text{O}_6$, is successfully worked for potassium in Italy by means of hydrochloric acid. Greensand of New Jersey (Odessa, Del.), shales in Wyoming and other states, and feldspar contain potassium. The nitrate deposits of Chile contain potassium, and there is now recovered a 25 per cent KNO_3 material, by means of a special process; in case of necessity, this method of working could be applied to all the Chile nitrate produced, and with normal production, approximately 300,000 tons a year of potassium nitrate could be obtained. Other deposits are in Spain, Abyssinia, Canada and Russia.

In 1935, 76.4 per cent of the world production of potassium salts from minerals or brines was the German-French one, and of that production, the United States imported 13.9 per cent.

Aside from minerals and brines, potassium salts are obtained by collect-

Heat exchangers are used everywhere, utilizing the heat of vaporization of vapors from the crystallizers, heats of solution of various salts, and other heats. This is one of the outstanding examples in the country of the practical application of solubility diagrams, phase rule, and other physico-chemical data.

See furthermore *Ind. Eng. Chem.*, 10, 839 (1918).

The American Trona Corporation is now the American Potash and Chemical Corporation, 70 Pine St., New York.

^{6a} *Chem. Met. Eng.*, 42, 430 (Aug., 1935).

⁷ *Chem. Abstracts*, 13, 2737 (1919).

⁸ *Ind. Eng. Chem.*, 10, 838 (1918).

ing the flue dust which passes out of cement kilns,⁹ by means of a Cottrell precipitator; it is estimated that 2 to 5 lbs. of K_2O may be recovered for each barrel of cement made. For iron blast furnaces, similar installations indicate that 17 lbs. of K_2O may be conserved for each ton of pig iron manufactured. The ashes from fermented molasses residues, ashes from the spent pulp of the sugar beet (7000 tons yearly), wool washings, and kelp⁹ are commercial sources of potassium compounds.

Potassium nitrate may be used for fertilizing; it has the advantage of combining two of the essential elements. Formerly the extraction of potassium nitrate from the upper layer of the soil near stables was of some importance (India); the constant re-formation of nitrate is due to the growth of bacteria. Potassium nitrate may be made by double decomposition of potassium chloride with sodium nitrate: $KCl + NaNO_3 = KNO_3 + NaCl$. Solid potassium chloride is added to a strong hot solution of sodium nitrate; sodium chloride first separates; then on cooling, potassium nitrate crystallizes. Another method is to pass nitrogen peroxide into potassium chloride solution.¹⁰

In the Kooban province in southern Russia, extensive plantations of sunflowers furnish stalks which are ashed and then extracted for potash; the production is over 20,000 tons a year.¹¹

Potassium salts are also in demand in the chemical industries, for the reason that they crystallize well as a rule, whereas the sodium salts do not. As a result, it is easier to separate potassium compounds from other reaction products than it is to separate the corresponding sodium compounds. Purification by crystallization is also easier for potassium compounds than for sodium compounds. Examples of potassium salts manufactured on an industrial scale in preference to the sodium salts merely because the former crystallize with ease, are potassium permanganate, dichromate, chlorate, and ferrieyanide. In some cases, the potassium compound is preferred because the corresponding sodium compound is hygroscopic; in still others, because of the specific action of potassium, which differs from that of sodium.

The United States imports potash salts; in 1940, 274,473 tons of salts were imported, with a content of 115,241 tons of K_2O . The domestic production from all sources was 658,249 tons of salts, equivalent to 379,677 tons of K_2O . In 1941, and this year, 1942, imports have ceased, except for small shipments from Chile, such as 8000 tons of potassium-sodium nitrate. The estimated supply available from domestic sources is stated as 533,000 tons K_2O , sufficient for domestic needs.

TABLE 16.—*World production of potash in metric tons (1938) (Minerals Yearbook for 1940). Figures for more recent years are missing.*

Germany	1,861,000
France	581,790
United States	287,532
Poland	108,352
Palestine	29,059
U. S. S. R. (1937) 266,000

⁹ *Ind. Eng. Chem.*, **10**, 834 (1918).

¹⁰ *Ind. Eng. Chem.*, **23**, 1410 (1931).

¹¹ *Chem. Met. Eng.*, **30**, 501 (1924).

NATURAL ORGANIC FERTILIZERS

By-products of the packing industry which are of value as fertilizers are dried blood, bone meal, and tankage. The fish industry contributes fish scraps. In a number of other industries there are by-products which serve primarily as cattle feed, but if, for any reason, they are unacceptable for that purpose, they may be of value as fertilizing agents.

In the slaughter house, the blood is pumped to a coagulating tank with a central bottom. It is cooked until coagulated, and of the consistency of liver. On standing a few hours, a separation takes place; water settles out at the bottom and is drawn off. The coagulum is pressed, dried, and powdered; it forms a dark, reddish meal. It is either sold as such, or mixed with potash salts and phosphates to make a rich fertilizer.

Bones are cooked in open tanks, or steamed under pressure; in either case, grease is removed. The degreased bones are crushed and powdered.

Tankage is used primarily for feeds; it is a brown meal, containing 0.5 to 11 per cent nitrogen as NH_2 and 12 to 20 per cent of bone phosphate of lime. Applied to the soil, tankage decomposes more slowly than dried blood. Fertilizer tankage is produced from meat scraps, intestines, bones, and carcasses of dead or condemned animals, by cooking under a steam pressure of 40 lbs. for 4 to 12 hours. Grease and tallow float to the surface and are removed; the solids are separated from the tank water, and ground. The tankage still contains 10 to 20 per cent grease which is generally removed by naphtha, before it is sent out as a fertilizer.

Guano is a mixture of birds' excrements and fish bones and other fish refuse, found on certain islands off the Peruvian coast, where the rainfall is slight. The deposits are surface deposits and are still in process of formation, but their importance as to tonnage has decreased. Their quality has also decreased as the materials rich in urea and ammonium oxalates are practically exhausted. Guano is found and mined in other localities.

A nitrogenous material is produced from activated sludge in sewage disposal plants; such a material is Milorganite, described in Chapter 13.

SYNTHETIC UREA

A nitrogenous material of synthetic origin is synthetic urea $\text{NH}_2 \cdot \text{CO} \cdot$

NH_2 ; in solution its formula is more probably $\text{HN}:\text{C} \begin{array}{c} \nearrow \text{NH}_3 \\ | \\ \text{O} \end{array}$. Its nitrogen content is remarkably high, namely 46.6 per cent for the pure substance. It is being manufactured in Germany and in the United States on a large scale. The suitability of synthetic urea as a plant food is just as good as that of the natural urea in manures.

The process of Carl Bosch and Wilhelm Meiser¹² consists in passing the mixed ammonia and carbon dioxide gases, with some moisture, into an autoclave held at 130° to 140° C. (266° to 284° F.); ammonium carbamate, $\text{NH}_2 \cdot \text{CO} \cdot \text{ONH}_2$, forms first, and is transformed into urea. (Fig. 48.)

¹² U. S. Patent 1,429,483.



*ammonium
carbamate*



urea

The conversion is about 40 per cent, and there is discharged from the autoclave, continuously if desired, a melt which is introduced directly into plate still. Steam enters at the base, and drives out the uncombined ammonia and carbon dioxide, while a solution of urea is discharged at a bottom of the still. It is concentrated and crystallized.



FIGURE 48.—Synthetic urea storage pile, at the Leuna Works, Germany.
(Bourke-White Photo from Pictures, Inc., New York.)

The make-up gas may be conveniently introduced by running a solution of ammonium carbamate into the upper part of the column; the gas drive out is compressed in warmed compressors and conveyed by warmed line to the autoclave, to prevent the deposition of ammonium salts.

The Krase process¹³ provides for the introduction of liquid ammonia and liquid carbon dioxide into an autoclave. Modifications¹⁴ provide for neutralizing unchanged ammonia with phosphoric acid, producing a concentrated fertilizer containing two of the essential elements.

The figures in Table 17 will indicate the relative importance of several fertilizer materials.

¹³ "A direct synthetic urea process," by H. J. Krase, V. L. Gaddy and K. G. Clark, *Ind. Eng. Chem.*, 22, 289 (1930).

¹⁴ U. S. Patents 1,797,095; 1,782,723.

TABLE 17.—Importance of fertilizer materials (1939).
(Bureau of the Census)

	Tons	Value
Fertilizer industry, all products		\$185,684,328
Complete fertilizer (mixtures containing nitrogen, phosphoric acid, and potash)		
Superphosphates	5,088,468	117,666,262
made for sale	4,152,642	
Bone meal	2,757,340	23,937,433
Tankage	62,004	1,760,942
Other fertilizers	225,275	6,325,415
Fish scrap, 1935 figure	360,146	6,660,877
	100,211	2,655,591

The average price for muriate of potash (50% K_2O) in 1940 was \$23.54 to \$26.75, according to season; sulfate of potash, \$31.90 to \$36.25; manure salts (30% K_2O), in bulk, \$15.84 to \$18.00; kainite (20% K_2O), \$10.75 to \$12.75.

The developments in the nitrogen industries are part of a study of the general field of fertilizers; these developments have been presented in Chapter 6, and many statements and figures of primary interest to the fertilizer field are included there.

OTHER PATENTS

U. S. Patent 2,074,880, molecular addition compound of calcium sulfate and urea, $CaSO_4 \cdot 4CO(NH_2)_2$, made by reacting mixtures consisting of calcium sulfate dihydrate and urea in a saturated aqueous urea solution. The following U. S. Patents have been assigned to the Tennessee Valley Authority: 2,037,306, on manufacture of ammoniated superphosphate; 2,040,081, agglomeration of fine phosphate rock; 2,013,328, manufacture of dicalcium phosphate; 2,044,774, treating phosphate rock to eliminate fluorine.

PROBLEMS

1. What is the highest percentage of K_2O which any potassium chloride preparation can contain?

2. One hundred tons of mineral containing 59 per cent of carnallite pass through the refinery and are made into crude potassium chloride containing 48 per cent K_2O . If the recovery is 72 per cent, how many tons of crude potassium chloride will be obtained?

3. Fixed nitrogen in the form of 96 per cent urea totaling 1000 metric tons of nitrogen are ordered. How many pounds of material will have to be shipped? Make the same computation for commercial ammonium sulfate, Chilean nitrate, assuming for each 96 per cent purity.

4. 2000 pounds of rasorite carrying 85 per cent $Na_2B_4O_7 \cdot 4H_2O$, are dissolved, filtered, and run to the crystallizer as a 25 per cent solution of borax, $Na_2B_4O_7 \cdot 10H_2O$, at 150° F. After cooling to 100° F., the crystals are centrifuged and go to the drier carrying 5 per cent moisture. The mother liquor contains 8 per cent borax. What yield of dry crystals is obtained?

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The manufacture of portland cement has become an important industry; in 1940 the production was 21.18 million tons, for the United States. Compared to the same year tons mined by the extent of 3.7 million tons, while the total produced was 4.89 million tons. These three industries are now recognized as essentially chemical.

Chapter 9

Portland Cement, Lime, and Gypsum Plaster

The tremendous expansion of the portland cement¹ industry in the last twenty years is due to extensive road-building programs, to the development of reinforced concrete construction, and to the adaptability and uniformity of the material. Cement roads are permanent, and their upkeep practically nil. Reinforced concrete permits the construction, for instance, of a horizontal platform bridging the space between two walls, capable of carrying heavy loads without other support than itself. Not only walls and piers, but girders of concrete are now freely used. Bridge piers, tunnels, dams, and canal walls are built of concrete as well as sidewalks, steps, garage and factory floors, and building foundations. One reason for the almost universal use of portland cement is the comparative ease of working it (pouring); another is its strength, which increases with age; a third is its uniformity, which permits calculations of strength as reliable as those made for structural steel.

Portland cement is a greenish-gray, impalpable² powder. Its essential constituents are lime, silica, and alumina, which are combined to form tricalcic silicate, $3\text{CaO} \cdot \text{SiO}_2$, tricalcic aluminate, $3\text{CaO} \cdot \text{Al}_2\text{O}_3$, and dicalcic silicate,³ $2\text{CaO} \cdot \text{SiO}_2$; these are unstable compounds, which on being wetted, rearrange with different speeds. Tricalcic silicate acts rapidly, forming gelatinous calcium hydrate and gelatinous silica, and to this change is due the initial set which occurs in 3 hours; the hydration continues, the gelatinous material binding the grains of sand which are always added, and the crushed stone filler, to a hard mass. Tricalcic aluminate acts with the same rapidity as tricalcic silicate, but does not produce a strong bond. Dicalcic silicate acts only after months have elapsed.⁴ The hardening of portland cement continues for years, and the concrete made from it increases in strength. As time passes, the gelatinous calcium hydrate crystallizes, adding a further element of strength.

In mixing water with portland cement and stones, to give the concrete, 4 to 8 gallons of water are used per sack of cement; not more than $2\frac{1}{2}$ gallons will chemically combine with each sack of cement, to become part of

¹ The name was given by Joseph Aspdin, because the cement he made in 1824 yielded stones resembling those quarried near Portland, England; his cement was the prototype of the present portland cement.

² No grains can be felt between the fingers.

³ There are four forms of dicalcic silicate, all of which occur in portland cement. The major one, however, is $\beta\text{-}2\text{CaO} \cdot \text{SiO}_2$.

⁴ The complete statement regarding the constituents of portland cement will be found in "Properties of the calcium silicates and calcium aluminates occurring in normal portland cement," by Bates and Kott, *Technical Paper 78*, Bureau of Standards, Washington (1917). Two thorough articles on the subject are: E. S. Shepherd and G. A. Rankin, *Ind. Eng. Chem.*, **3**, 211 (1911), and G. A. Rankin *ibid.*, **7**, 466 (1915).

the structure. The rest evaporates. Too rapid evaporation is undesirable; it is retarded by keeping the surface covered with straw, and by wetting (curing). The purpose of curing is to prevent evaporation until after hydration has proceeded well along to completion.

The setting of pure portland cement is so rapid that, if it were uncontrolled, the cement would be useless; the addition of small percentages of calcium sulfate (as gypsum) gives the desired retardation. The initial set of pure cement occurs in 6 minutes; 3 per cent of gypsum lengthens the period to 3 hours.

In the manufacture of portland cement the proportions of lime (generally as limestone), alumina, and silica (as clay or shale) are carefully adjusted; for example, 77 per cent limestone, 23 per cent shale, and the mixture is sintered; in natural cements a suitable rock is generally used without admixture, so that the composition is variable, and there is no sintering. Considerable amounts of portland cement are made from the iron blast furnace slag.

Portland cement sets under fresh water as well as in air, it is therefore also a "hydraulic" cement; for sea water, its iron content should be raised to several parts per hundred.

Raw Materials. Limestone and clay are the necessary raw materials; pure limestone is not usually chosen, except for adjusting the final mixture; rather argillaceous limestones, which are more common and which can neither be used for making quicklime, nor in a blast furnace, are used. The "cement rock" is such a limestone, which contains the necessary constituent in proportions so nearly right that only slight adjustments are necessary. The plant is erected as near to the deposit as possible; the rock is hauled perhaps 1000 to 2000 feet in the most favorable cases.⁵ The material is blasted in the quarry,⁶ and brought to gyratory crushers,⁷ which reduce the rock to egg size. The addition of correcting amounts of limestone, for example, takes place at this stage. The properly mixed materials are generally dried in a short (40-foot) rotary furnace with inside heating, then crushed further in a swing-hammer mill,⁷ sieved, and finally pulverized in a Raymond suction mill,⁷ or similar pulverizer. The material ready for the furnace is of such fineness that 90 per cent will pass through a 100-mesh sieve. The relative proportions of raw materials must be such that the analysis of the final cement falls between the following limits:

		Limits	Per cent	Average
Lime	CaO	58-65		61.5
Silica	SiO ₂	20-25		22.5
Alumina	Al ₂ O ₃	4-11		7.5
Magnesia	MgO	0-4		2.0
Iron	Fe ₂ O ₃	0-4		2.0
Sulfur trioxide	SO ₃	0-1.75		1.0
Alkali	Na ₂ O, K ₂ O	0-3		1.5

Instead of limestone, marl, a deposit of a geologically more recent origin, may be used; in such a case, it is often conveyed, wet, through pipes to the

⁵ Examples: Bath, Nazareth, Martin's Creek, near Easton, Pa., and Alpha, just across the river in New Jersey.

⁶ Which may be a hill, such as at Martin's Creek.

⁷ Chapter 44

ant, and ground wet; the clay is then also ground wet. In one large plant with wet mix, the raw materials are ground in 8-foot diameter by 30-foot long 3-compartment Campbell mills, turning at the rate of 19 r.p.m.; 93 per cent must pass through 200 mesh. In three plants, oyster shells and clay are the raw materials. After mixing and settling, the materials are shaped into bricks which are dried before they are sent to the furnace, or the slurry may be fed directly into the kiln, to be dried by the outgoing gases; in the latter case the furnace is lengthened. Both wet and dry grinding are the practice in the United States, with the 152 operating plants (1940) about equally divided. Limestone and clay is the most frequent combination, roughly 3 parts of limestone to 1 of clay.

During the furnacing carbon dioxide and water of constitution are lost, so that there is a shrinkage in the material obtained; it is usually estimated that 1.7 tons of raw materials produce 1 ton of cement.

The slag from the iron blast furnace may be so adjusted that it is well suited for the manufacture of portland cement; it is mixed with limestone, with perhaps another addition to reach the desired percentages, and furnaced as the rock mixtures are. The shrinkage in this case is somewhat less.

By froth flotation the raw materials may be purified from micas, tale and sulfides which form the concentrate, which is discarded, while the calcite, quartz and composite rock particles are the tailings. The flotation agents are aliphatic amines, in quantities much below 0.4 pound per ton of feed.

TABLE 17a.—*Distribution as to raw materials of the 1935 production of portland cement in the United States.**

	Per cent of total
Cement rock and pure limestone	31.0
Limestone and clay or shale	58.8
Marl and clay	1.9
Blast furnace slag and limestone	8.3

* Bureau of Mines, Statistical and Economic Surveys.

The Portland Cement Rotary Furnace. The furnace generally used in the United States is a brick-lined steel cylinder, slightly inclined from the horizontal; it is mounted on idling wheels of small diameter, and carries a gear wheel meshing with a pinion wheel which rotates the cylinder at the rate of one-half to two r.p.m., according to size. The operation is continuous; raw material is fed in at the upper, colder end, and the clinker is discharged at the lower, hot end. The flame is formed by pulverized coal, atomized oil, natural gas, and sometimes producer gas, at a burner placed in the stationary hood into which the lower end of the cylinder fits. The hood acts also as receiving box for the discharged material, called the clinkers. An extension of the stationary box reaches into a smaller cylinder inclined from the horizontal in the opposite direction, and also rotated; as a result, the clinkers, after reaching the smaller cylinder through the chute, move forward toward the discharge opening. A current of air sweeps over the clinkers and enters the burner hood, there to become the air of combustion for the fuel; by preheating the air in this way, the temperature reached in the hotter end of the furnace is raised, while the clinkers are cooled.

The size of the kiln has been gradually increased.⁸ The kilns studied and used as models in this account are 11 feet in diameter and 250 feet long. The kiln is inclined $\frac{3}{4}$ -inch to the foot, toward the hot end, which is also the clinker discharge end. The feed, in this instance a slurry feed, enters at the colder and upper end. There is a lining of bricks at the hot end which is 9 inches thick for 100 feet; then a lining 7 inches thick for 110 feet; over the last 40 feet the shell is bare, except for lifters. The kiln is rotated by a girth gear at the rate of 0.6 r. p. m. The rated maximum capacity for each kiln is 2100 barrels a day (at 376 lbs. each); the usual rate is nearer 1500. The output is varied by varying the amount of feed. The clinker is delivered to a tubular cooler similar to the kiln, but only 90 feet long and 9 feet in diameter. The fuel is powdered coal, here 88 pounds to the barrel of cement, which is considered a good performance; 100 and 120 pounds is not uncommon. A mill near Montreal is said to burn only 60 pounds of coal to the barrel. The secondary air is preheated in the cooler; the flue gas is 20 and even 35 feet long. The temperature in zone A (Fig. 49) is moderate;

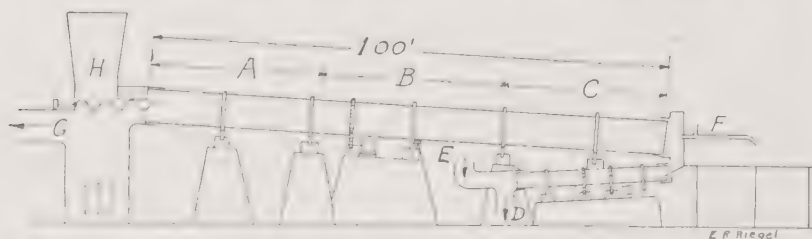


FIGURE 49.—The rotary portland cement furnace; *F*, pulverized coal burner; *H*, feed bin with conveyor; *D*, discharge of clinkers; *G*, passage for fire gases to boilers and stack; for zones *A*, *B*, and *C*, see text.

ate; here the moisture is driven out and the materials heated. In zone B, the middle zone, the temperature averages 1800° F. (982.2° C.); the carbon dioxide is expelled from the limestone. In zone C, the maximum temperature of 2800° F. (1538° C.), which may be increased to 2900° F. (1593° C.) or dropped below if desired, is developed. The clinker is discharged at the hot end in a stationary hood with discharge piece leading into the cooler. The gases pass from the feed end to an electrical precipitator and thence with temperature between 900 and 1100° F., through a 15-ft. diameter stack 235 feet high to the atmosphere. A pound of slurry travels through the kiln in 6 hours.

The average fuel consumed per barrel of cement produced was as follows (1940): coal, 119.5 pounds; oil 0.2174 barrel of 42 gallons; natural gas 1.56 cubic feet.

In Europe the Lepol kiln has been developed;* it operates with a fuel consumption of 45.6 pounds of coal per barrel of clinkers. In 1932, there were 34 Lepol kilns in Europe, one at San Sebastian in Spain.

⁸ In 1935, there were 193 kilns 125 feet long, 176 between 150 and 199, and 94 between 200 and 260. 9 were between 261-299, 8 between 300 and 350, and 8 between 372 and 400 feet in length, the maximum was 400. 35 were as short as 40 to 60 feet. "Fuel efficiency in cement manufacture, 1909-1935," W.P. and Bureau of Mines, report E-5, April 1938.

⁹ "Cements, Limes, and Plaster," by E. C. Eckel, New York, John Wiley and Sons, Inc., 1928.

* Report by the inspection committee, "New cement burning process," *Rock Products*, 35, 42-47, 1932.

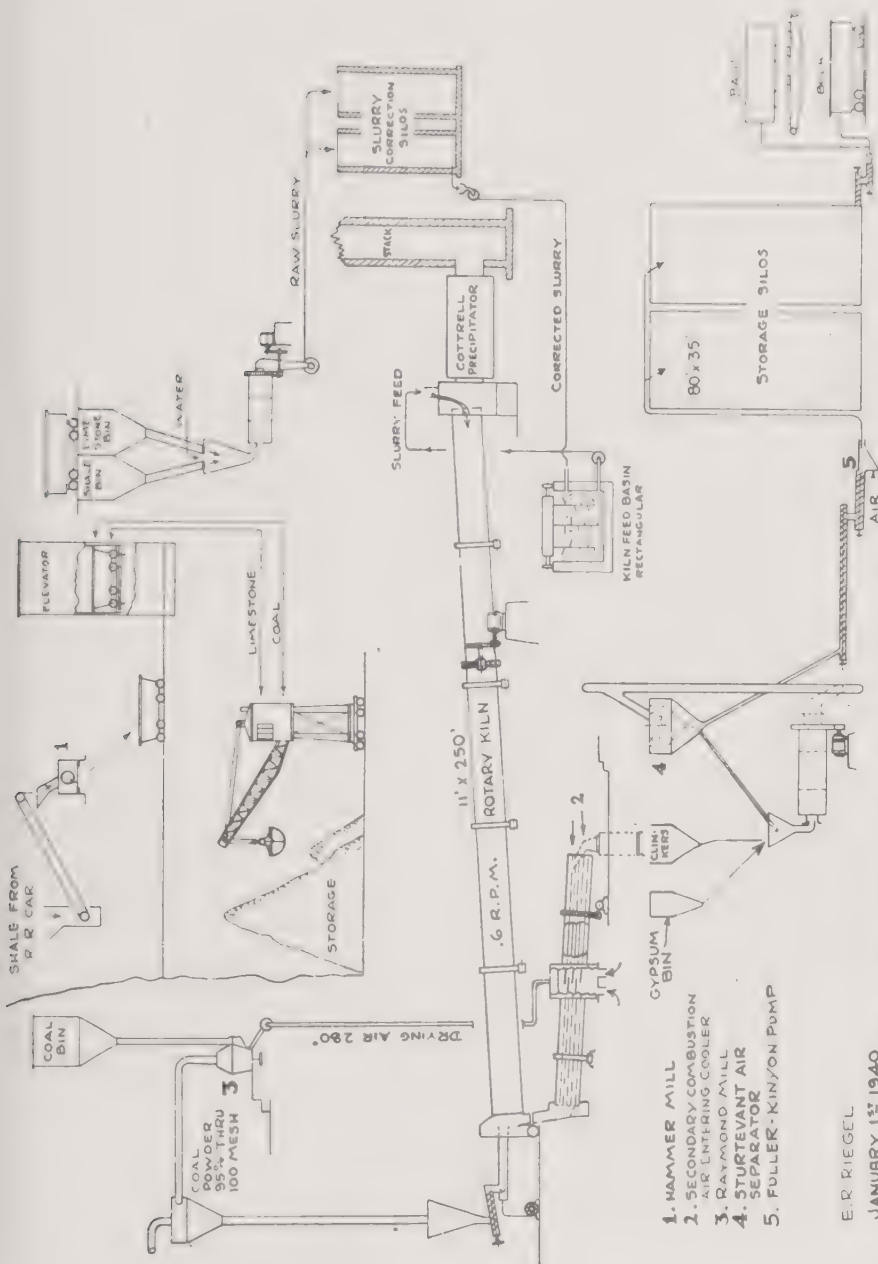


Figure 49a.—Pictorial flow sheet for a portland cement plant with wet mix.

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The volume of the charge is such that over the greater length of the kiln it forms a coating about 18 inches thick. At the burning zone, it seems much higher. A sort of nose is built up by the moving charge, and it seems that it must crash forward toward the hot end, yet it does not. In the last few feet of the kiln, this coating is about 6 inches. In the hot zone there is no melting to form a fluid, but merely a softening to a dough-like mass, in which there is nevertheless a liquid phase, which is estimated to make up 2 per cent of the whole. The clinker produced is homogeneous, consisting of a hard mass with numerous gas pockets; from the kiln studied, the clinker is quite uniformly $\frac{3}{4}$ -inch in diameter, and black. It is considered good practice today to form the hottest zone as close to the discharge as possible. The hot spot, for example, may be 35 feet and, the highest temperature 1 foot from the clinker discharge end; the result is a rapid chilling of the clinker as it is discharged, so that the magnesia in the liquid phase does not have time to form the crystal, periclase; instead all the liquid phase becomes a harmless, and in some ways a beneficial glass. Periclase is avoided because it is the main cause for "delayed expansion," a property tested for by the autoclave test. Normal cement may have a "delayed expansion" of 0.1 per cent; special cements 0.02 to 0.04 per cent.

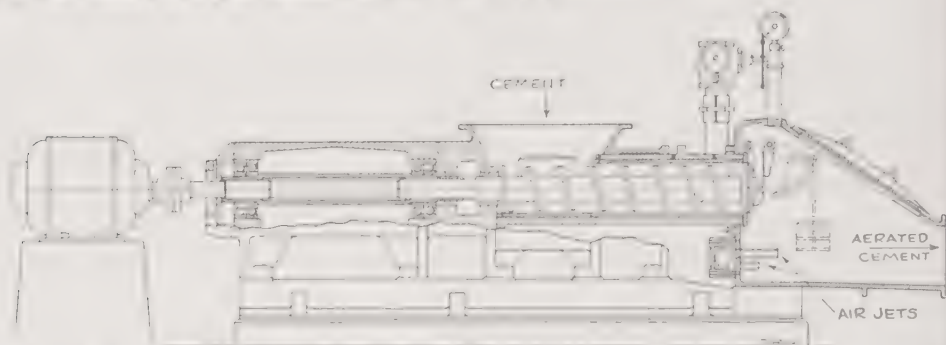


FIGURE 50.—The Fuller-Kinyon pump for conveying portland cement. The screw feeds the cement powder into aeration chamber, where the air jets deliver a stream of compressed air which unites with the powder to form a fluid mass which travels 600 feet laterally and then 95 feet vertically to the top of storage silos.

The clinker is ground in various ways; one of the more modern device is a three-compartment Compeb ball mill; the product goes to an air separator which returns the tailings for further grinding. Cement is moved by a Fuller-Kinyon pump, a Robinson air-activated conveyor, or other means, to storage silos, and thence to a bagging machine, or to bulk loading. In this particular plant, it takes 592 pounds of raw materials to make a barrel of cement of 376 pounds; hence the shrinkage is 36.5 per cent.

The fineness of the powdered cement is a matter of importance. It is still customary and useful to speak in terms of mesh fineness, as for example portland cement tests 98 to 99 per cent through a 200-mesh sieve, and 90 per cent through a 325-mesh sieve. However, the fineness may also be expressed in terms of "specific surface," that is, the surface in square centimeters of one gram of cement.* The test is performed by dispersing 0.

* Federal specification SS-C-158, September 30, 1936; and SS-C-191a, same date.

gram of the powder in 15 cubic centimeters of kerosene; 6 drops of oleic acid are added, and the whole is then dispersed further in 335 cubic centimeters of kerosene. The turbidity is measured at various levels by means of the light transmitted, as recorded by a photoelectric cell. For normal portland cement, the New York state requirement is 1750 specific surface. The Federal requirement is 1500.

*Approximate size distribution of an average portland cement
with the rate of hydration.*

Size in microns	Percentage of total	Color	Time required for complete hydration
Under 10	21	pure white	less than 24 hours
10-20	16	white	24-48 hours
20-30	8	nearly white	4 days
30-43	30	very light brown	7 days
44-70	16	brownish gray	28 days or more
Over 74	9	gray	indefinite

200-mesh is equivalent to 74 microns, 325-mesh to 43 microns.

Concrete, 38, No. 4, p. 16 (1931).

Portland cement meets specifications and additional tests which have become official.¹¹ The neat (unmixed) cement must have a tensile strength of 500 lbs. per square inch after 7 days; the cement mixed with 3 parts of sand must have a strength of 200 lbs. after the same period.

The strength of concrete, which is composed of cement 1000 lbs., sand 1500 lbs., and crushed stone 3000 lbs., is greatly increased by imbedding in it twisted square steel bars, or wire netting similar to stout fencing; it is then called reinforced concrete.

Magnesium fluosilicate,¹² $\text{MgSiF}_6 \cdot \text{H}_2\text{O}$, in solution, is applied to the surface of cement roads and walls to protect them from weathering; such protection is not absolutely necessary, for the cement structure is permanent without it; but the surface becomes smoother and the weather-resistance properties are increased. Pipes for sewers, as large as 5 feet in diameter, are made of concrete, and are harder and stronger if treated with magnesium fluosilicate solution.

The recovery of potash from cement furnace gases is discussed briefly in Chapter 8.

The high early strength of portland cement, a property possessed by the normal cement, may be increased by finer grinding or by raising the calcium oxide content to obtain a high ratio of tricalcic silicate to dicalcic silicate (such as 7 or 8 to 1, instead of the normal 5 to 4). In the manufacture of *high early-strength portland cement* either of these two methods or both may be employed to obtain the desired result. The sieve test may be 99.5 per cent through 325-mesh; the specific surface must be not less than 1900.*

Other *special cements* are listed below. The aluminous cement resists the action of sulfate-bearing waters.¹³

¹¹ "Standard specifications and tests for portland cement; adopted by the American Society for testing materials, and by the U. S. Government," 1917, 47 p., obtainable (10 cents) from the Superintendent of Documents, Washington, D. C. But. Foreign and Domestic Commerce, Industrial Standards, No. 1.

¹² Chapter 2.

* Federal specification SS-C-201.

¹³ Ind. Eng. Chem., 18, 554 (1926).

*Composition of normal and modified portland cement
(In percentages)*

	Normal	High early-strength	Low heat	Aluminous
CaO	64	65	60	40
SiO ₂	23	20	23	5
Al ₂ O ₃	6	6	5	40
Fe ₂ O ₃	3	3	5	15
MgO	2	1.5	2	.1
SO ₃	2	2.5	2	.1

*Production figures for normal and special portland cements for 1940.**

Special cements:	Barrels (376 lbs.)
High early-strength	4,471,297
Low heat	8,422,707
Portland-puzzolan	413,870
Masonry	219,480
Oil well	711,348
Sulfate-resisting	193,348
Miscellaneous	580,502
Normal portland cement	130,216,511
Total	145,229,063

* Minerals Yearbook.

The average price at the mill in 1940 was \$1.46 a barrel for normal portland cement, \$1.87 for high early-strength portland cement.

LIME

Lime is the oxide of calcium, CaO, and is obtained by calcining limestone. The reaction $\text{CaCO}_3 \rightleftharpoons \text{CaO} + \text{CO}_2$ is reversible, but it may be run completely to the right by removing the carbon dioxide from the system; this is done in the kiln by the fire gases on their way out. Limestone is calcined in two main types of kilns, the vertical or shaft kiln, and the horizontal rotary kiln.

The shaft kiln is illustrated in Figs. 50a and 50b; limestone is fed in

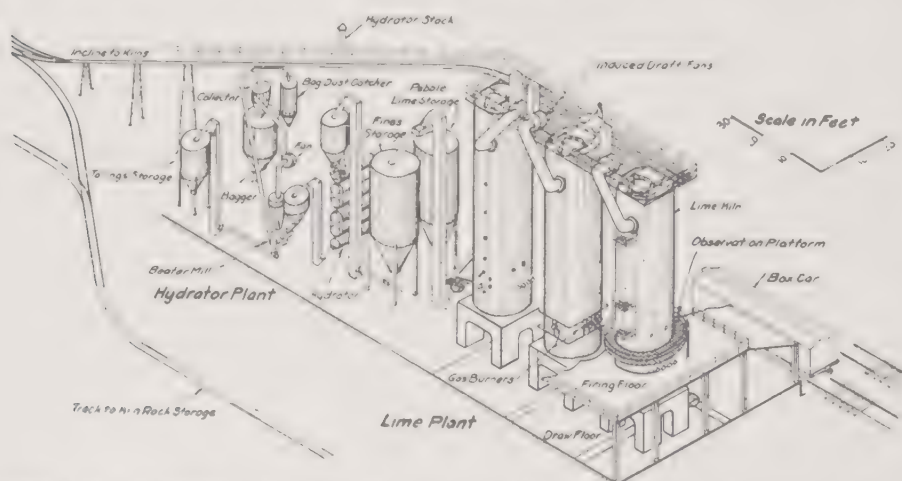
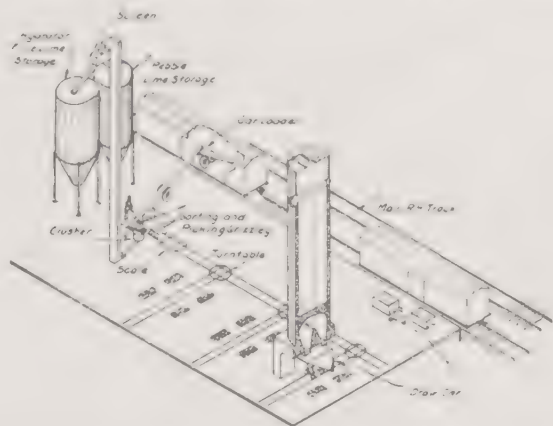


FIGURE 51a.—Isometric drawing of three gas-fired lime kilns with sealed tops. The induced draft fans return exhaust gas, to temper and lengthen the gas flame. The exhaust gas leaves the kiln at a temperature between 700 and 800° F. The kilns are about 60 feet high. Hydrator plant is shown. (*Rock Products*, p. 86, January 15, 1935; plant designed by Mr. Victor J. Azbe.)

At the top, the fire gases enter at a short distance from the bottom, and the hottest lime is drawn out at intervals, or continuously, at the bottom. The temperature may be 1000°C . (1832°F .) in the kiln proper; it will be lower

FIGURE 51b.—Plan of lime handling system with kiln cut away to show inner construction.



at the exit, because the gases preheat the entering charge. The carbon dioxide passing out may be recovered; it may be returned, at least in part, to the burners in order to temper and lengthen the flame, and the balance wasted. Too high a temperature is avoided because it tends to harden the lime by fusion of impurities. The maximum capacity of a shaft kiln is reckoned generally as one ton per square foot of shaft area per day, so that a kiln with shaft 9 feet by 7 feet, with about 60 square feet area, will produce 50 to 60 tons of high-grade lime per day. The shaft kiln is a heat exchanger as well as a reactor; the solids traveling down take heat from the gases which are rising; the operation illustrates the counter-current principle. The fuel¹⁴ may be natural gas, producer gas, oil, wood, or coal; in the latter case, the modern construction places the coal in outside fireplaces, admitting only the fire gases. The lime leaving the kiln is crushed to the size required, and screened.

Lime may also be calcined in a rotary kiln similar to the cement kiln but generally smaller, consisting of a steel shell lined with refractory bricks, set near the horizontal. The fuel may be those enumerated for the shaft kiln, with the addition of the increasingly favored pulverized coal. A rotary kiln handling pebble lime may be 135 feet long, 8 feet in diameter, making 1 revolution in 95 seconds; the pebbles are discharged at red heat, 1660°F . (904.4°C .) while the furnace itself may have a temperature of 2500°F . (1271°C .). A drag conveyor and a bucket elevator bring the hot pebbles to a rotary cooler, from which they pass to the shipping containers. It is interesting to note that the general shape and size of the pebble is preserved, so that grading of the calcite pebble may be done in Michigan, for example. The pebbles transported to the site of the kiln (Buffalo), and there calcined, without further grading. The kiln described furnishes 72 tons of lime per day, operating continuously; one ton of coal is burned for $2\frac{1}{2}$ tons of lime produced—a greater consumption than that in the shaft kiln. In the

¹⁴ "Burning lime in a gas-fired continuous kiln," by W. D. Mount, *Chem. Met. Eng.*, 20, 428 (1919).

latter, 12 per cent coal on the weight of the product is very good practice; the theoretical consumption is 11.2 per cent. It will be evident that in efficient fuel utilization, the shaft kiln leads.

TABLE 18.—*Analyses of limestone and the lime produced from it in a rotary kiln.*

	Stone taken from feeder at No. 1 kiln	Pebble lime from dis- charge end of cooler
Loss on ignition	43.68	0.22
SiO ₂56	1.02
R ₂ O ₃48	.68
CaO	54.66	97.04
MgO51	1.10
Sulfur138	...
SO ₃03
CaCO ₃	97.55	...
MgCO ₃	1.07	...
Available CaO	94.76
30-mesh residue24

Not infrequently the same company will have both shaft and rotary kilns, the shaft kiln for large stones, the rotary for fines.

A pebble of lime, when treated with a limited amount of water, develops heat, swells, and soon disintegrates into a fine powder consisting of hydrate lime. $\text{CaO} + \text{H}_2\text{O} = \text{Ca(OH)}_2$. Much of the lime produced is changed into

TABLE 18a.—*U. S. production of lime (1940).**

	Short tons	Price per ton
Quicklime	3,501,104	\$6.69
Hydrated lime	1,385,825	7.59
Total	4,886,929	6.95

hydrated lime, for agricultural purposes and others. Lime serves for many purposes; it is as useful as an alkali as sulfuric acid is as an acid in the chemical industries. It is used in mortar, plaster, insecticides, refractory bricks, in metallurgy, in the paper industry, for water treatment, and for hundreds of other purposes.*

TABLE 18b.—*Consumption of lime in the several kinds of uses (1940).**

	Short tons	Price per ton
Agricultural	364,823	\$5.71
Building	1,010,435	8.45
Chemical industries	2,643,762	6.20
Refractory	867,909	7.98

* Minerals Yearbook.

GYPSUM PLASTER

Gypsum plaster is made by removing most of the water of crystallization from gypsum, $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$, by gentle heat; the plaster so produced when mixed with water, may be spread and shaped, and in a few hours it sets to a hard mass. Gypsum plaster is almost universally used for coating the inner walls of dwellings. It is often called plaster of paris, because huge

* See I. C. 6884R, "Lime," by Oliver Bowles and D. M. Banks, revised by Duncan McConnell, Bureau of Mines, October, 1941.

deposits of gypsum are found in Paris and in its neighborhood, and these were the first to be worked.¹⁶

While limestone is found exposed or covered by an overburden easily stripped off, permitting open pit operations, gypsum generally occurs at greater depths and shaft operations are the rule. It may be said also that limestone is far more common than workable gypsum deposits. This is partly because only rock with the composition $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ may be used; if it contains less water, calcining it does not produce a material which sets with water. A seam 3 feet in thickness is considered valuable, if it has a reasonable extent; the deposits near Buffalo have such thickness and have an area roughly of 1 square mile.¹⁷ The depth at which they lie averages 20 feet. The method of mining is by entries, and "rooms," 250 feet deep and 35 feet wide.¹⁸ Holes are drilled by electric augers; 20 per cent dynamite is used for blasting, and is exploded by a fuse. The broken rock is loaded into the mine cars which are pulled by an electric (D. C.) locomotive to the shaft or incline. Gypsum rock is nearly white, and has large crystals; it is a soft rock. Gypsum mines do not require artificial ventilation.

The mine cars are dumped into a gyratory crusher¹⁹ with a pot 11 feet deep; the product is elevated to a rotary screen, which separates the fines from the lumps, which are about egg size. The fines are shipped to portland cement plants.²⁰ The lumps are fed to a rotary drier, a horizontal steel cylinder 30 feet long, with internal firing; the rock is passed through so fast that it attains a temperature of only 150° F. (65° C.). The dried rock is more easily crushed further and pulverized; the devices used are a swing-hammer mill¹⁹ followed by inclined flat screens; the material which passes through the screen is sent to a Raymond suction mill;¹⁹ the tailings (on the screen) are returned to the swing-hammer mill. The pulverized material from the Raymond mill is sent to the calciners, upright cylindrical vessels with slow-moving agitators, and several horizontal flues through which fire gases pass. The fine powder remains in the calciner 1 hour; the temperature is about 350° F. (177° C.); no more than three-quarters of the water of crystallization is removed. After calcining, the powder is white; it is discharged through a door at the base of the calciner which leads to conveyors; these bring the material to the storage house.

Calcined gypsum is made into wall plaster by the addition of asbestos, hair, shavings, sweepings from packing houses, and dextrin, according to specifications. Without addition, it is plaster of paris. Considerable amounts are used at the mill itself to make plaster boards,²¹ which may then be placed on the walls of dwellings with little labor, and by any one unskilled in plastering. The manufacture of these plaster boards is largely automatic. The calcined rock is mixed with 8 per cent (by weight) of selected sawdust on a conveyor which passes into a shallow tank where it takes up the right amount of water for setting. The wet mass is dumped on a sheet of paper,

¹⁶ It was the study of gypsum plasters which led the French chemist, Le Chatelier, to his investigation of the constitution of portland cement.

¹⁷ Akron, Scottsville, Oakfield, and Clarence, New York.

¹⁸ Compare coal mining in Chapter 12.

¹⁹ Chapter 44.

²⁰ See the first part of this chapter.

²¹ Examples: "Best Wall," "Sheet Rock."

leveled, and covered by a second sheet; the edges are folded over, and the sheet pulled continuously toward the knife; by the time it reaches it, 10 minutes have elapsed. The board may now be handled, although it is not dry. The knife cuts it in appropriate lengths; these are dried in tunnels, by a stream of warm air, while suspended vertically to avoid warping.

TABLE 19.—*Gypsum products in the United States in 1940.**

	Short tons	Price per ton
Uncalcined		
Portland cement retarder	820,828	\$ 1.96
Total	929,119
Calcined		
Building uses	3,580,467	13.82
Industrial uses	3,704,110	13.59

* Minerals Yearbook.

Gypsum plaster is valuable for making casts; on setting, there is a 1 per cent increase in volume and as a result, the casts are sharp. For temporary buildings imitating famous examples of architecture, such as for the International Exposition in Paris (1937), gypsum plaster is used in vast quantities.

An artificial gypsum has been mentioned in Chapter 7.

MAGNESIUM OXYCHLORIDE CEMENTS

This name is given to cements made by adding a strong solution of magnesium chloride to magnesium oxide, usually called calcined magnesia. A filler such as small stones, wood flour, or cork, is mixed into the paste. After a short time the paste sets to a hard mass approximating portland cement in strength. The proportions of solution and magnesium oxide must be properly chosen and strictly observed. The cement, after setting, takes high polish; it is used only for interior work such as floors in hospitals and public buildings. Sorel cement is a magnesium oxychloride cement.

OTHER PATENTS

U. S. Patent 2,069,164, rotary kiln; 2,217,685, flotation concentration for calcite.

PROBLEMS

1. Since three-quarters of the water of crystallization of the gypsum is removed during calcination, show that the finished material retains 6.2 per cent water.
2. A lime kiln delivers 27 tons of lime per day; how much limestone must be fed in, assuming both substances to be pure and the burning perfect?
3. The amount of fuel per barrel of finished Portland cement is given in the text (an average). For a furnace producing 215 tons of cement per day, how many tons of coal must be provided?
4. A Portland cement contains its calcium silicates in the proportions of 5 tricalcium silicate molecules to 4 dicalcium silicate. Compute the absolute amount of the basis of 23.46 per cent SiO_2 in the Portland cement. How much lime (CaO) must be added to change the ratio of the calcium silicates to the new one, namely 8 molecules of tricalcium silicates to 1 of dicalcium silicate? How much limestone is required, if it contains 95 per cent CaCO_3 ? All the lime added will react with dicalcium silicate. What is the limestone quantity to be added in terms of the original Portland cement?

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- "Universal Atlas plant at Leeds, Ala., firm's only wet-process operation," W. E. Trauffer, *Pit and Quarry*, 32, p. 32, with a layout on p. 34 (1939).

The great importance of ceramics to the chemical industries is evident when it is pointed out that the steel shells of portland cement furnaces, Bessemer steel converters, of sulfite pulp digesters, of gas producers and water-gas generators are lined with bricks; in addition, fire boxes and boilers, reverberatory furnaces for varied purposes, and tank furnaces for glass depend for their proper construction upon ceramics. These are only a few examples and leave out of reckoning building bricks and stoneware.

Chapter 10

Ceramic Industries*

Ceramics is the art of producing useful articles entirely or chiefly from raw materials of an earthy nature by high-temperature treatment during manufacture. The principal raw material is clay, which may be used alone or with the addition of other substances. Some of the more important products of the industry are: ordinary building brick and tile, sewer pipe and electrical conduit, drain tile, refractory bricks of all kinds, electrical and chemical porcelain and stoneware, white ware such as dinnerware, chinaware, floor and wall tile, porcelain enamels and abrasives. Sand bricks bonded with lime do not belong under ceramics, but, nevertheless, will be treated briefly after common bricks.

Clays differ in many particulars, especially in their plasticity, which in turn depends upon their content of admixed organic matter, upon their state of hydration, and upon the fineness of the subdivision of the particles. A plastic clay is called a fat clay; a less plastic one a lean clay. Plasticity is really the resultant of two separate properties: deformability, which allows shaping, and tenacity, which resists tearing. In drying and firing the clay body (for certain clays, not for all) contracts so much that the article would develop cracks and be useless; the shrinkage is reduced by the admixture of a non-shrinking substance such as clay itself which has been calcined. For calcined clay loses its plasticity and at the same time its shrinkage. Another non-shrinking admixture is ground flint (SiO_2). In general, the lower the proportion of clay the weaker the article; the more plastic the clay, the harder and stronger the article after drying and firing, and the greater the shrinkage. Clays are included in the substances studied from the standpoint of the colloidal state (colloid chemistry).

Another property of clays which is of great importance is their fusibility, which differs according to their impurities, geological history, and substances purposely admixed. Clays fuse less, the greater their content of aluminum silicate $\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2 \cdot 2\text{H}_2\text{O}$; the addition of some metallic oxides renders them more fusible while other oxides render them less so. Examples of the former are iron oxide and titanium dioxide; of the latter, aluminum and chromium oxide (Cr_2O_3).

In general, clays have been formed from decomposition of rocks by various agencies through time. If the clay remains at the original location

* In collaboration with Mr. William Horak, B.S. in Ceramic Engineering (University of Illinois), Consulting Ceramic Engineer, Hartford, Conn.

is a primary clay, usually white, with a low content of iron so that it burns white; it is called *kaolin* or *china clay*. It might be said that kaolins are the product of the weathering of feldspar, either potash feldspar, $\text{K}_2\text{O} \cdot \text{Al}_2\text{O}_3 \cdot 6\text{SiO}_2$, or soda feldspar, $\text{Na}_2\text{O} \cdot \text{Al}_2\text{O}_3 \cdot 6\text{SiO}_2$; the alkali has been washed away. They would then be termed primary clays, and this is true enough if the statement is qualified by adding that some kaolins, such as the Florida and Georgia kaolins, are transported, and hence are of secondary origin. If, in the course of geological changes, the clay has been transported by water, glacier, or wind to another location, it is a secondary clay¹; it has lost the undecomposed, coarse particles of feldspar which remain in certain primary clays of that origin, but it now contains limestone powder, hydrated oxide mud, and organic impurities, in varying amounts. In general most of the clays other than white clays are of secondary origin, but here are exceptions here too, as for example the red-burning clays of Washington and Oregon, which have been formed by the weathering of basalt rock. The purer deposits of the secondary clays are more plastic than china clay, and are used under the name of *ball clays*.

The plasticity of a clay may be increased by aging, that is, storing it damp, or by exposing it to the action of the weather; the process is partly one of hydration accompanied by gelation, and partly a bacterial action which has as one of its results the further subdivision of the particles. Whiteware bodies are aged after filter-pressing by stacking the cakes one on top of another in damp cellars or bins. Clays are also washed for certain uses, and levigated to free them from coarse particles.

The analytical figures for a high-grade china clay and a secondary clay are given in Table 20.

TABLE 20.—Analysis of china clay and secondary clay.

	China clay* washed free from admixed quartz	Secondary clay**	Kaolin $\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2 \cdot 2\text{H}_2\text{O}$
Silica SiO_2	47.5%	50.33%	46.5%
Alumina Al_2O_3	37.4	27.06	39.5
Iron oxide Fe_2O_3	0.8	2.29	
Iron oxide FeO		2.62	
Lime CaO	trace	1.22	
Magnesia MgO	0	3.34	
Soda Na_2O	1.1	1.78	
Potassium oxide K_2O		4.40	
Water H_2O	12.48	6.66†	14.0

* From *China and Clay Industries of Connecticut*, by G. F. Longfellow, State of Conn., State Geological and Natural History Survey, Hartford (1905), p. 47.

** *Ibid.*, p. 59.

† Includes all loss on ignition, organic matter as well as water.

THE MANUFACTURE OF WHITEWARE

Whiteware, such as dinnerware, electrical porcelain, chemical porcelain, floor and wall tile, is generally made from a mixture of clays and other substances. Usually these consist of kaolins² (china clay), ball clays, feldspar, and flint. The proportion of each of these depends upon the uses to which

¹ River deposits are called fluviatile or alluvial, lake deposits lacustrine, and sea deposits marine.
² *China* is preferred, but as it does not soften below 1700° C. [3022° F.] so that it is infusible at the kiln temperature; ball clay to hold water; flint for whiteness, rigidity, and to reduce shrinkage; feldspar as the flux or binder.

the ware will be put. Other materials which may be added are talc (steatite), whiting (CaCO_3), or magnesite (MgCO_3).

Dinnerware represents a large portion of the whiteware field; it is made by one of two methods, which are also the ones used in all the other branches of porcelain manufacture; these are casting and jiggering.

Making the Slip. The proper amounts of the clays are weighed out and stirred in a blunger with water which may (but need not) contain electrolytes to disperse the clays until most of the lumps are broken up. The other substances, such as feldspar or flint, are then added and the whole stirred until thoroughly blended. The "slip," as the mixture is now called, is of a thin, creamy consistency and flows readily. It is allowed to run from the blunger through a vibrating screen, which removes bits of wood, metal, and lignite, and thence over a magnetic separator to remove iron particles which would stain the fired ware.

Clay Body is Filtered and Aged. From here, the slip flows to filter presses³ where it is separated from the water and forms cakes containing 1 to 30 per cent of water. The cakes are stored in damp cellars where they are allowed to age, or they may be used immediately for making up the casting slip. As a general rule, only the body to be used for jiggering is aged. The aging process improves the plastic properties of the clay body and insures even distribution of moisture in the mass.

From this point on, the body is made into ware either by the casting process or the jiggering process.

Casting Process. The clay body from the filter cakes or aging bins is placed in blungers with about 35 per cent water and the proper amount of electrolytes, usually a mixture of equal parts of sodium silicate and sodium carbonate, in amount sufficient to give the desired fluidity to the slip. The clay body and water are thoroughly mixed, again screened (clawed) and run over a magnetic separator. The mixture now has the consistency of not too heavy cream, and flows readily; it is termed the "casting slip" and is ready for use.

Casting Slip run into Molds. Plaster of paris molds having for the inside of the form the dimension and lines of the outside of the object to be cast are at hand. They are filled with slip, and let stand for 15 to 30 minutes and then the excess slip is poured out. The plaster of paris absorbs the water, and the clay body is left as a lining of the mold walls, exactly reproducing them. After the excess slip is poured off, the mold is allowed to drain and is set for a period of 20 to 45 minutes in a warm place. At the end of this time the clay lining has set and shrunk sufficiently to allow its removal from the mold; the latter is used over again.

The cast ware is then trimmed and dried in hot-air driers, after which it is fired. In some plants, and for some wares, a glaze coating is applied to the dried ware and both body and glaze are fired together. In general, however, a separate firing is given before and after glazing, known in the first case as the bisque firing, and in the second case the gloss firing.

Jiggering Process for Tableware. In making ware by "jiggering" or "jollyng," the clay body from the storage bins is fed into a pug mill and

tempered with enough water to give a stiff-mud consistency. From the pug mill it is forced by augers through a die in the form of a cylinder or "wad."

The "wads" are ready for use and are distributed to the jiggerman. The jigger consists of a rotating unit carrying a mold which will form one face of the ware while the tool forms the other face. For tea cups, which are made without handles (these are cast in "gangs" and fastened on later), the

FIGURE 52.—Cross-section through plaster of paris form for shaping clay cup.



mold forms the outside of the cup, and the tool the inside. For plates, the inner surface (later, the upper) is formed by the mold, and the bottom surface by the tool. Oval platters are made on a jigger having eccentric motion.

To make each object, a piece from the wad of just the right size is thrown in the center of the rotating mold and the tool brought down on it, spreading it over the mold and cutting away the excess clay. The tool is of metal and has a profile shape of the form desired on the surface it makes. During this operation the jiggerman keeps the clay-tool interface lubricated with water. The formed ware is placed with the mold in the drier. After drying, the ware is taken off and treated like the cast ware. The dry molds are returned to the jigger.

This process is much more rapid than the casting process and is used wherever the shape of the object does not prohibit it. It can be used for all simple shapes which contain no bulges or reverse curves.

The Saggars. In order to protect the ware from soot and dust during the firing, it is packed in clay boxes called saggars. Each box is open; they are piled on one another from the base of the kiln to the top, and the second box closes the first. The saggars are of various shapes and heights, to fit the ware. For example, one sagger can hold 4 piles of 20 plates each; the lowest plate rests on a thick form, the setter, which is used over and over; it prevents deformation of the lowest plate when it softens. The other plates are supported each by the next lower one, separated by flint granules, known as "bitstones."

The making of new saggars is a constant operation. The materials are broken saggars ground to a coarse grain, about 4 to 8 mesh, and fines; new clay, untreated in any way, and water. The mass is mixed in a pug mill, which cuts and mixes the dough-like mass, and discharges it into an extrusion machine which forces it out in the shape of a loaf of bread. This is cut in lengths of 16 inches or so, and one length is placed under a press which forms the saggars at one stroke between the descending die and a steel box. After firing, the saggars are ready to be used, and serve several times; when cracks in the side develop, they must be discarded. The use of saggars made of silicon carbide grain in place of fireclay grog is increasing.

The Pottery Kiln. The ware packed in the saggars is ready for the firing, which is done in one of a number of kilns, circular in cross-section, built of bricks, about 12 feet in diameter and 12 to 14 feet high inside. The kiln is

built of common bricks outside, and of firebricks inside, and is surmounted by a stack. Each kiln has 6 to 8 small fireboxes at the base, whose fire gases enter the inner chamber at circumferential openings, and in addition at one central opening in the floor. To provide room for the fireboxes and necessary channels, the floor of the kiln is about 4 feet above the room floor (ground). The saggars are so arranged in the firing chamber that 5 "quarters" result, and within these quarters, the circulation of the fire gases may be regulated by means of empty saggars with suitable sections knocked out. A column of saggars set one on top of another in the kiln is called a "bung."

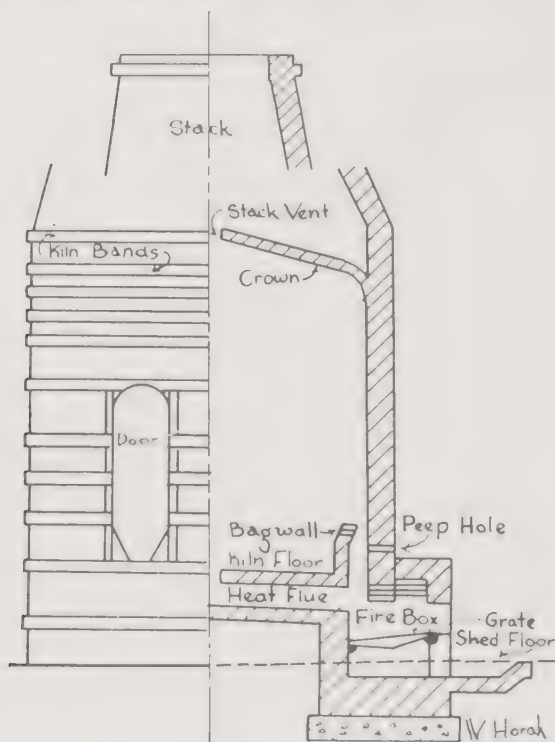


FIGURE 53.—Sketch of a typical pottery kiln. The ware is placed in saggars and these are set in the kiln in vertical rows called "bungs." The fire gases are directed upward by the bag walls in part, while another part is drawn to the center of the kiln by flues and ascends through the ware.

The fire gases leave the kiln through a stack vent in the crown and from there to the stack proper, which surmounts the structure. By these means the temperature may be so controlled that there is a difference of 15°F (8°C .) between the top and the bottom. The heat is raised very gradually. The temperature at various points is observed by means of pyrometric cones (or Orton cones) ⁴ sighted through peepholes at various levels. The time of actual firing is about 66 hours; including cooling, unloading ("drawing") and reloading, the cycle is 1 week. The maximum temperature is 2300°F (1260°C .) for whiteware generally; porcelain may go to $2500\text{--}2550^{\circ}\text{F}$ ($1371\text{--}1399^{\circ}\text{C}$). At each packing the kiln is filled to capacity, about 220 dozen pieces. The ware shrinks 10 to 15 per cent, depending on the composition. The fuel is coal, gas, or oil, with coal the most common, although gas and oil are not rare, since the ware is high enough in price to allow the use of the dearer fuel.

⁴ Chapter 48.

The product from this first firing is the biscuit ware, strong, nonporous, and white; the second or glass firing is at a lower temperature and shorter. There are a few potteries which fire low at the first firing and high at the second.

A modified procedure has recently been developed which will have far-reaching, beneficial effects. The air remaining in the plastic clay, as it leaves the pug mills, is removed by the application of a vacuum. It is found that such de-aired products are stronger for a given thickness of wall than untreated ware, or as strong with a smaller wall thickness. Some clays which previously could not be used give satisfactory results when de-aired. The same wall thickness, with firing at a lower temperature than previously, gives as strong a ware.⁵

Decorating and Glazing. For under-glaze decorations, the biscuit is brushed with shellac, and the pattern transferred to it by means of decalcomania paper. The pigments are so selected that the color obtained after firing is the desired one; the first color from the transfer paper is immaterial. Very elaborate designs covering the whole plate in some cases may be applied by means of decalcomania paper. Hand painting is also practiced, and a combination of decalcomania and hand painting. The decalcomania paper may be made in the pottery itself, from an etched plate coated by the proper pigments, and applied to a strong but thin paper first treated with a soap solution.

The decorated pieces are passed into a suspension of the glaze; they retain enough to cover them. Next they are dried and packed in saggers again, but this time they must not touch; they rest on three pegs set in the wall of the sagger.⁶ The saggers are fired at a lower temperature for 30 hours only. The glaze is more fusible than the biscuit, and no deformation takes place. Overglaze decoration is less durable.

The glaze must be transparent for underglaze decoration, and must not react with the colors of the decoration so as to change the shade, or cause them to run together; it may be opaque for overglaze decoration; it must have approximately the same coefficient of expansion when heated as the under body, so that it will not "craze" or peel off. One formula includes sodium oxide, borax, zinc oxide, silica, tin oxide, calcium carbonate, and lead oxide; it produces an easily fused, non-transparent, white glaze.

There are various kinds of tableware bodies; the more important ones are real porcelain, strong and non-porous (red ink makes a slight stain); semi-porcelain, less strong, somewhat porous (red ink makes a deep stain.)

Stoneware is made from clays not selected for color, although in some cases the color is pleasing; it is fired at a temperature approaching that at which porcelain is fired. The ware is not packed in saggers, and the glaze is applied by means of salt, introduced at the top of the fire in the firebox toward the end of the firing period. Sewer pipe and glazed conduit are "salt glazed" in the same way. The salt melts and attacks the surface of the ware just enough to make it run. Stoneware is cheaper than porcelain, except in a

⁵ "The effect of de-airing stiff-mud bodies for clay products manufacture," by J. O. Everhart, C. R. Austin, and W. C. Rueckel, *Ohio State University Studies, Engineering Series, Bull. 74* (1932), in cooperation with the Bonnot Co., Canton, Ohio.

⁶ The marks of the three pegs may be seen on the under side of almost any plate.

few cases when for artistic merit the ware brings as much as porcelain. Earthenware has a porous body; it is fired at moderate heat, insufficient to cause complete vitrification; if the ware is to be water-tight, it must be glazed. There are many products which occupy intermediate places, so that a classification is difficult. Chemical stoneware is generally brown in color and fired without saggars, but it is made with great care. Certain pieces such as the Cellarius vessel⁷ have surprisingly thin walls, so that cooling may be rapid; yet they are strong. Other pieces are used chiefly for storage of acids, and are as large as 6 feet in height; the walls are then made thicker.

Electrical insulators of the umbrella type, for high-tension currents, are made of a clay mixture similar to the kind used for fine tableware. A large unit is about 10 inches across and 6 inches high; it is shaped in a mold for its one side, and with a tool on the jigger wheel for the other. The units are dried, packed in saggars, loaded on kiln cars, and fired in a tunnel kiln.

The insulator units are glazed. After firing, they are tested for resistance to high-voltage current, as well as in a number of other ways. Twenty units set up one in the other offer enough resistance to prevent a million volt current from passing.

Tunnel Kiln. The tunnel car kiln is aptly named, since it is a tunnel built of firebrick through which cars carrying the ware to be fired are made to travel. It is divided into three zones: (a) the preheating zone, where the cars enter and the ware is preheated by waste heat from the cooling zone; (b) the firing zone, wherein the ware is brought to the desired temperature

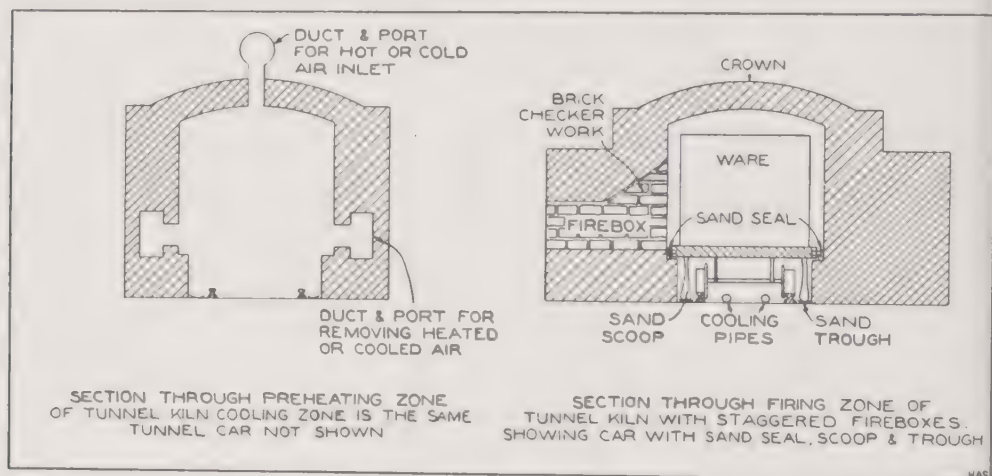


FIGURE 53a.—The tunnel kiln, as used in ceramics.

and (c) the cooling zone. The firing zone portion is the only zone equipped with fireboxes, and it is wider than the preheating or the cooling zone for that reason. The usual fuel is oil, but coal, gas, and even electricity have been used successfully. In the cooling zone, outside air is introduced at the top exit end and drawn by fans through the ware to a point near the firing zone where they are exhausted at the sides at a point about level with the

⁷ Chapter 3.

car tops. The air thus heated by the ware is carried by pipes to the pre-heating zone where it can give up its heat to the incoming ware.

The size of tunnel kilns varies considerably; the length depends upon the particular ware to be fired, especially upon the size of the individual pieces. Larger pieces require a longer kiln. Tunnel kilns have been built as big as 400 feet long and as small as 24 feet long. The length of the zones varies two ways: with the length of the kiln, and with the particular heat treatment the ware may require.

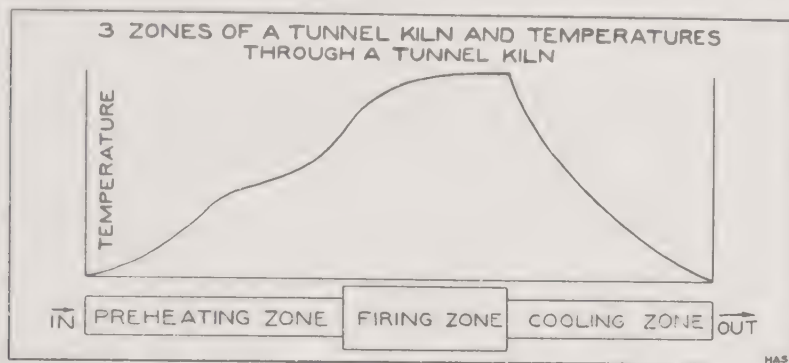


FIGURE 53b.—The heating, firing and cooling zones in a tunnel. The temperature designation is left out purposely, as it will differ for the several wares.

Not only straight tunnel kilns, but circular ones are built; in the latter, the entrance end is close to the exit end.

The cars are moved through the tunnel by various types of "pushers"—rams operated hydraulically, pneumatically, or mechanically—or by a chain under the cars.

The tunnel kiln is used for all kinds of ceramic products, not merely for electrical insulators. It has come into favor because it saves labor, packs faster, saves heat, and even more important, because the temperature prescribed is more definitely reached for uniform periods over all of the ware—that is, the firing is more uniform.

Color and Luster. Iridescent ware (luster ware) is produced by exposing the hot ware to the vapors of stannous chloride or ferric chloride. Iridescence combined with color is produced by applying a mixture of silver sulfide and clay, and exposing to a smoky (reducing) flame.

Gold gives its characteristic color over the glaze. In general the decorating colors are not simple oxides but complex calcines. The colors which some metal oxides give when used in the glaze are listed below. It is worth noting that the famous chinese red glazes are colored with copper.

Cobalt oxide produces	various shades of blue
Copper oxide produces	greens and reds
Chromium oxide produces	greens and reds
Iron oxide produces	yellow to brownish red
Uranium oxide produces	yellow to orange red
Gold chloride produces	pinks
Manganese oxide produces	shades of violet

BUILDING BRICKS

The familiar red brick is made from a secondary clay containing in the neighborhood of 4 per cent iron oxide as a natural impurity. If the clay is rich, that is, relatively pure, sand, crushed rock, or cinders must be added^{*}; a less pure clay, a "mild" clay, which contains gravel or sand, is preferable. For the cheapest good bricks, the dry material must pass through an 8-mesh screen; for finer grades, a 20-mesh screen. The density of the brick depends mainly upon the method of working; a wire-cut brick, not re-pressed, would be the lightest; on placing it in a mold and pressing it by a screw-operated die, it becomes denser, as well as more accurate; power pressing will raise the density still further.

Stiff-mud Process for Heavy Clay Products. This process is widely used for making building brick, tile, paving brick, some terra cotta, conduit, drain tile, and for some types of firebrick. A variation of the process here described is used for making most sewer pipe.

The clay as it comes from the pit or storage bins is ground in dry pans and carried to a pug mill, where it is tempered with the proper amount of water to give a stiff, mud-like consistency. From the pug mill it is forced by an auger screw through a steel die of the shape and size desired for the finished ware. The clay issues from the die head as a continuous column. A few feet from the die head, a cutter, generally automatic, consisting of piano wires set at proper distances on a jig (movable frame), cuts the column into the right lengths. The cut raw ware continues on a belt conveyor, from which it is picked and set on a drier car. Full cars of bricks, with 1,000 to 2,000 bricks per car, are pushed into driers and left to dry according to a predetermined schedule for the particular clay used. From the driers, the cars are taken to the kiln yard; the dry ware is taken off and set in the kiln, usually of the down-draft type, for firing.

The Round Down-draft Kiln. The down-draft kilns are built as large as 40 feet in diameter and 12 to 19 feet from the floor to the top of the crown. The one shown in Figure 54 has eight fire boxes around its circumference. The heat and combustion gases from the fire boxes are directed upward toward the crown and are reflected by the crown downward through the ware; the gases pass through slots in the floor into the collecting flues and center well hole, and finally through the main flue to the stack. The firing temperature varies considerably; in the case of a dense red brick, to give an example, the maximum temperature will lie between 1470° and 1650° F. (800° to 900° C.).

By careful setting of the ware and skillful firing, the temperature distribution may be made uniform throughout. This type of kiln is periodic in operation; it is fired by coal, oil, or gas, but mostly by coal.

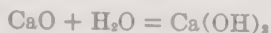
After firing, the bricks are sorted; those with perfect shape, color and correct dimensions are No. 1 bricks; less perfect ones are grouped together as seconds; insufficiently burned ones are added to the new charges. The price of wire-cut red bricks, of first quality, is about \$18 to \$25 a thousand.

Sand-Lime Bricks. In districts without clay resources, bricks which approximate in strength the common red bricks are made from sand, or

^{*}The rich clay without addition would shrink and crack badly when fired.

crushed sandstone (by-product of a sandstone quarry) mixed with about 8 per cent of carefully hydrated lime.

Quicklime is treated with the proper amount of water.



in an iron box; there is produced a light fluffy powder which is screened and stored in silos to insure complete hydration. It is mixed with sand and enough water to give a dough which may be shaped in presses. The new bricks are loaded on small trucks and pushed into autoclaves, where they

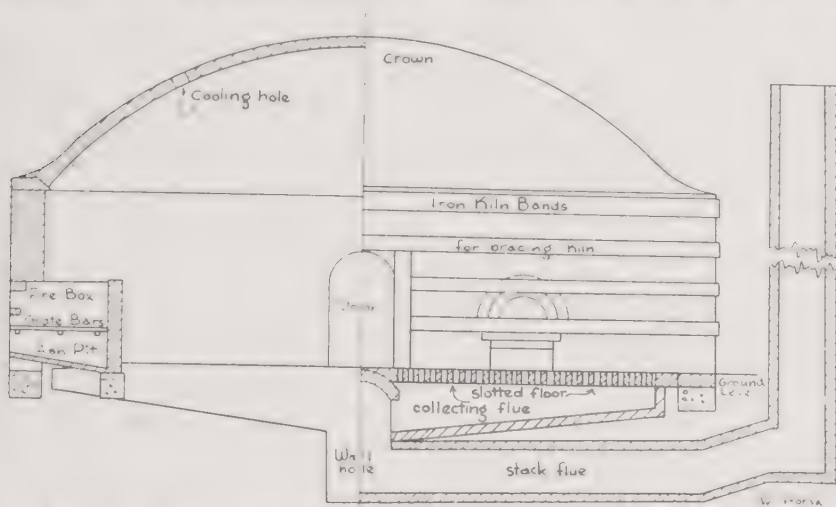


FIGURE 54—The round down-draft kiln, suitable for firing heavy clay products. (See text.)

are subjected to the action of steam at 125 pounds pressure; this operation is called "curing" and corresponds to the firing of the red bricks. Usually bricks are shaped in the daytime and cured over night. The bond between the sand particles is monocalcium silicate.⁹ The price of sand-lime bricks is about the same as that of common bricks.

FIREBRICKS

Firebricks are the material for the construction of open-hearth steel furnaces, for iron and other blast furnaces and stoves, for cupolas, calciners, and many other types of chemical engineering apparatus; they serve to line fireboxes and furnaces, and to fill regenerators. The materials are a fire-clay made even less plastic than it normally is by preliminary firing at high temperature followed by crushing and known as "grog"; and a smaller proportion of a more plastic fireclay to furnish the bond. The firing is done at a temperature of 2500° F. (1371° C.), or somewhat higher. The burned brick is cream-colored, or light buff; it is generally softer than common brick, but may also be as hard or even harder. Firebrick cost about \$40 per thousand, for low heat duty brick, up to as high as \$900 to \$1000 for some high-grade super-duty brick.

⁹ "Manufacture and properties of sand-lime brick," W. E. Emley, *Bureau Standards Tech. Paper*, 85, Washington (1917).

There are many kinds of refractories; the primary objective is to produce a shape or brick which will resist the attack of metals, slags or glass at high temperatures without appreciable distortion or softening. Another objective is to produce bricks or shapes for high-temperature insulation; such bricks do not resist abrasion and slagging. They are used as a backing to a first course of slag-resisting bricks. The insulating bricks are generally very light in weight; "cork brick" is an example.

The nature of the raw materials will depend upon the intended use. Silica will be selected for bricks which must be acid-resisting, but silica bricks are also used for heat conducting, in by-product coke ovens, for instance. Basic bricks, which resist basic charges, are made of magnesite bonded only by water, under great pressure, or by bauxite or alumina. There are also neutral bricks, such as chromite, graphite, and silicon carbide. In metallurgy, the nature of the slag determines the class of refractory to be used; thus a siliceous slag requires an acid refractory. For crucibles which must conduct heat as well as resist high temperature, natural graphite¹⁰ bonded with 30 per cent clay and some water glass is largely used. Silicon carbide bonded with lime serves for muffles and electric furnace linings; clay-bonded silicon carbide is the general choice for high heat-conductivity brick; with graphite in addition, the mass becomes sufficiently elastic to form crucibles. An excellent high-conductivity crucible is made from silicon carbide¹¹ and tar; the carbon residue from the latter becomes the bond and is prevented from oxidizing during use by a glaze. Clay pots are used in the glass houses; they are purchased unburned by the glassmaker, who must burn them in his own furnaces.¹²

The highest-grade silica bricks are made of quartzite or ganister, and bonded by 2 per cent lime; they are generally heated twice, because they expand when heated (fireclay bricks shrink), and it is desirable that the expansion be complete before the wall or lining is built. The expansion is due to the change of quartz into cristobalite and tridymite, which are less dense forms of silica.

Much harm can be done by too rapid heating of the bricks in the process of manufacture; and the gradual cooling is just as important, for too rapid cooling causes strain and weakens the bricks.

For some years, refractories have been produced in the electric furnace.¹³ (Compare next chapter).

The fireclay refractories, priced at \$45 to \$55 a thousand (with shapes computed to the standard $9'' \times 4\frac{1}{2}'' \times 2\frac{1}{4}''$ brick), make up 75 per cent of all refractories; their distribution is 35 per cent to boiler linings and locomotives; 20 per cent to open hearth steel furnaces; 10 per cent to heat-treating furnaces and the like; 4 per cent to the glass industry; 4 per cent to the ceramic industry. As to composition, there are four types, a high silica (75 per cent), a high alumina (with 28 per cent silica), a high flint fireclay (40 per cent silica, 43 per cent alumina), and a plastic fireclay (52 per cent silica, 33 per cent alumina).

¹⁰ Formerly Ceylon graphite; now largely Madagascar graphite.

¹¹ U. S. Patent 1,356,939.

¹² Chapter 11.

¹³ Fred W. Schroeder, *Ind. Eng. Chem.*, 23, 124 (1931).

Refractories are tested for the temperature of deformation under load, linear shrinkage on heating, resistance to spalling on repeated heating and sudden cooling, and on resistance to three types of slag.

A few further particulars will be found in Chapter 45.

VITRIFIED ENAMEL OR PORCELAIN ENAMEL ¹⁴

"Vitreous enamel or porcelain enamels are fused silicate coatings applied to metal (usually cast iron or sheet steel).

"The first step in all types of vitreous enameling is the making of the frit." Proper proportions of raw materials such as feldspar, borax, soda ash, silica, fluorspar, cryolite, sodium nitrate and the like are thoroughly mixed and then fused in a smelting furnace. The melt is drawn off into water and the resulting friable product is termed 'frit.'

"The application of the enamel is accomplished by two general methods, the wet and dry process. In the former method the frit is ground in a pebble mill in the presence of water and clay to produce a workable suspension, or 'slip.' Opacifiers and coloring oxides are also added in the milling.

"The ware to be enameled by the wet process, after proper fabrication and cleaning, is coated by dipping it in the milled enamel followed by draining off the excess, or by spraying the slip onto the ware. In either case the enamel coating is dried and then fused in an enameling furnace. One or more coats are thus applied as may be required. The coat applied directly on the metal is usually of a special nature ¹⁵ to promote a firm adherence, while subsequent coats develop the desired color and texture.

"For application by the dry process, dried frit is ground to a fine powder in a dry mill, with the addition of the proper coloring oxides and opacifiers. The piece to be enameled receives a first coat by the wet process. The burnt first coat is not allowed to cool, however, but while the article is still hot the dry ground enamel powder is applied by means of a sieve. The piece of ware is then replaced in the furnace and the coat fused. To or more such applications are usually required to produce the desired results.

"Cast iron sanitary ware is usually produced by the dry process, most other ware by the wet process.

"Formerly all enamel plants produced their own frit. More recently large supply houses have marketed increasing amounts of frit to the smaller, and many of the larger enameling concerns. The frit as purchased by the enameling plant is ready for milling. Most of the frit thus purchased is for wet process enameling, in accordance with the above method.

"There is an increasing demand for enameled commodities as the merits of vitreous enamel become better recognized in a great variety of uses. Formerly the chief outlet was in the form of sanitary and cooking ware. Then came vitreous-enameled signs, stoves, refrigerators and dairy, canning and chemical equipment. The present rapid expansion involves a multitude

¹⁴ The quoted portion is the statement prepared especially for this chapter by Mr. Emerson P. Poste Consulting Chemical Engineer, Chattanooga, Tenn.

¹⁵ A ground coat is applied to cast iron and sheet iron, and fired; it must contain cobalt to promote the adherence to the metal surface; it is then dipped or sprayed with the cover coat, and fired once more (firing time 3 to 7 minutes). E. R. R.

Pyrometric Cones (Originally Known as Seger Cones)

Table of Fusing Points

Cone Number	When fired slowly 20° C. per hour		When fired rapidly 150° C. per hour		Cone Number	When fired slowly 20° C. per hour		When fired rapidly 150° C. per hour	
	° Cent.	° Fahr.	° Cent.	° Fahr.		° Cent.	° Fahr.	° Cent.	° Fahr.
Decorations	022	585	1085	1121	Electrical Porcelain	10	1260	1305	2381
	021	595	1103	1139		11	1285	1325	2417
	020	625	1157	1202		12	1310	1355	2435
	019	630	1166	1220		13	1350	1350	2462
	018	670	1238	1328		14	1390	1400	2532
	017	720	1328	1418		15	1410	1435	2615
	016	735	1355	1463		16	1450	1465	2669
	015	770	1418	1481		17	1485	1475	2687
	014	795	1463	1526		18	1485	1490	2714
	013	825	1517	1580		19	1515	1520	2768
	012	840	1544	1607		20	1520	1530	2786
	011	875	1607	1661		23	1580	1580	2876
	010	890	1634	1643		26	1595	1595	2903
	09	930	1706	1706		27	1605	1605	2921
	08	945	1733	1742		28	1615	1615	2939
Heavy Clay Products	07	975	1787	1814	Refractories	29	1640	1640	2984
	06	1005	1841	1859		30	1650	1650	3002
	05	1030	1886	1904		31	1680	1680	3056
	04	1050	1922	1940		32	1700	1700	3092
	03	1080	1976	2039		33	1745	1745	3173
	02	1095	2003	2057		34	1760	1760	3200
	01	1110	2030	2093		35	1785	1785	3245
	1	1125	2057	2120		36	1810	1810	3290
	2	1135	2075	2129		37	1820	1820	3308
	3	1145	2093	2138		38	1835	1835	3335
Art Pottery	4	1165	2129	2174	Clay Testings (PCE)*	39	1865	1865	3389
	5	1180	2156	2201		40	1885	1885	3425
	6	1190	2174	2246		41	1970	1970	3578
	7	1210	2210	2282		42	2015	2015	3659
	8	1225	2237	2300					
	9	1250	2282	2345					
White ware					Clay Testings (PCE)*				

and uses including parts for buildings. The future possibilities are almost unlimited.

The following may be taken as a typical white enamel for sheet iron:

White Frit	Per cent	Mill charge
Feldspar	29.5	
Borax	22.0	100 lbs. Frit
Silica	19.0	6% Clay
Cryolite	13.5	5% Tin oxide
Soda ash	3.5	
Fluorspar	3.5	
Sodium nitrate	3.0	
Antimony oxide	3.0	
Zinc oxide	3.0	

"As to colors, certain general facts may be stated: Red colors are usually made from iron, cadmium and selenium compounds. Greens are made from chromates or chromates properly combined with other mineral oxides. Yellow is produced from compounds of antimony, uranium and titanium. Blues are usually based on cobalt compounds, in combination with other mineral oxides to vary the color.

"There are three general ways of producing the desired colors. For the darker blues and black, coloring oxides are usually smelted in the frit. For certain other colors a relatively clear frit or glaze is used, the color and opacity being produced by mill additions. For the more delicate an opaque frit, such as given in the formula above, is used, and coloring oxides and varying amounts of opacifier are added at the mill."

TABLE 21.—*Production and total value for selected items in ceramics for the United States for 1939. (Bureau of the Census)*

		Value	Value per thousand
Red bricks, thousands	4,209,497	\$49,132,085	\$11.67
Buff bricks, thousands	515,976	7,685,985	41.42
Fireclay products, brick block or tile, thousands	506,570	25,125,126
High alumina brick, thousands	16,700	1,510,707	90.46
Plastic fire brick, in short tons	43,664	1,118,974
Glass house tank blocks, melting pots, floaters, rings, in tons	26,956	2,338,683
Clay refractories, including refractory cement, total	42,191,454
Porcelain electrical supplies	20,817,045
Sewer pipe and related products	18,295,679
Pyrometric cones	99,362
Chemical stoneware	722,139
Red earthenware	2,097,191
Whiteware	19,643,652
Hotel china	7,652,667
Saggers	607,502
Vitreous china plumbing fixtures	21,978,821

OTHER PATENTS

U. S. Patent 1,844,670, manufacture of an improved vitreous, acid-resisting enamel; 1,785,777, preparation of a slip for vitreous enamels consisting of an acid-resisting glass, titanium sulfate, and English pipe clay; 2,048,319, producing cast refractories; 2,069,059, method of producing ceramic ware; 2,235,881, acoustic tile; 2,207,911, mixture for vitrified ware; 2,230,206, dinner ware.

PROBLEMS

1. A kiln packed with saggars contains in all 2200 dozen pieces of tableware. Each piece weighs $\frac{1}{2}$ pound, and there are required 3 pounds of coal for each pound of ware fired. How many tons of coal are needed in all? With coal at \$4.00 a ton, what is the fuel charge against each dozen pieces?

2. A ware is made from a clay mixture which contains exclusively china clay, flint and feldspar. The feldspar in the batch is 22.5 per cent on the dry basis. The final ware contains 68 per cent SiO_2 . Taking the formula in the text as the composition of the feldspar, the composition of the china clay in the text as applying, and the flint as 100 per cent SiO_2 , how much of each raw material would you have to take for each 100 pounds of ware?

3. It is required to smelt $2\frac{1}{2}$ tons of frit for a white vitrified enamel of the formula given in the text. Assume a loss from all sources of 5 per cent. How many pounds of each of the materials listed will be required, if the loss is spread over all the items uniformly? It must be remembered that sodium nitrate and soda ash lose gas during the smelting as a normal reaction; in finding the theoretical yield, which may be done first, sodium nitrate and soda ash should be changed to their sodium oxide equivalent.

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It is essential that window glass should be an inexpensive commodity in order to permit its use in the most modest of dwellings. Ingenious improvements in its manufacture have made it possible to keep it low-priced in spite of the general increase in cost of labor and materials.

Chapter 11¹

Structural Glass, Glass Containers, Optical Glass, Special Glass

Structural glass includes window glass, wire glass, figured rolled glass, plate glass, glass blocks, and health glass; of these, ordinary window glass ranks first in the amount produced.

Window glass in the United States is made exclusively by mechanically drawing a flat sheet of glass, which passes through an annealing process as it is drawn and requires no subsequent annealing or flattening of any kind. Three processes are in use, which differ as follows: In the Fourcault process, the sheet forms in the slot of a clay block pressed into the glass melt by adjustable arms; it may very properly be said to be extruded. After being formed, the sheet is carried upward through the lehr, finally reaching the cutting platform above it. The original patent rights have run out.

In the Colburn process, the sheet is formed with the help of two edge guides in the glass melt; it rises vertically at first, then turns a right angle over rolls and travels horizontally through the lehr.

Finally, in the Pennvernon process (P. P. G.) the sheet is formed by a submerged clay block, and rises vertically through the lehr, as in the Fourcault process.

The molten glass for all three processes is obtained by heating together soda ash, lime, sodium sulfate, charcoal or other forms of carbon, sand, and cullet (broken glass), in a large trough-shaped furnace. Window glass is a soda-lime glass.

THE FOURCAULT PROCESS

Perhaps a fourth of the window glass made in the United States is made by the Fourcault process, modified more or less by each operating company's experience. The furnace has several small extensions called the work pits, in each of which one drawing machine operates. In order to have a definite furnace for study, the furnace of the Adamston Flat Glass Company at Clarksburg, W. Va., will be described, and all modifications given of the original Fourcault procedure will be those developed at the Adamston plant, one of the most successful of the many Fourcault units.²

The Furnace. The furnace is of the continuous type, with continuous feed, fired by gas, either natural gas, which is not preheated, or by producer gas, which is preheated. The combustion air is preheated in either case, by passing it through the regenerators located below the furnace.

¹ In collaboration with Mr. Donald E. Sharp, Ceramic and Glass Engineer, Research and Development Department, Hartford-Empire Company, Hartford, Connecticut.

² Studied through the courtesy of Mr. W. M. B. Sine, General Manager, and Mr. J. A. Voorhies, Plant Manager.

The plan of the furnace with the exact dimensions is shown in Figure 55. It is built of three kinds of bricks and forms: (1) silica bricks for the roof, or arch, commonly called the "cap"; (2) "refractory" blocks for those upright walls which do not come in contact with the molten glass; and (3) "flux" blocks, a special composition of fire-clays which resists glass attack and which is employed for those walls which come in contact with the

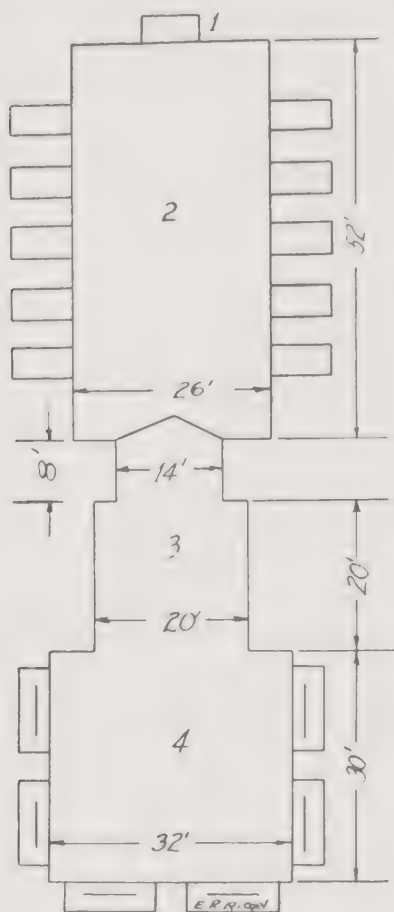


FIGURE 55.—Plan of furnace for window glass by the Fourcault machines. 1, the dog house, or charging trough; 2, melting end; 3, refining end, with neck between 2 and 3; 4, drawing chamber, surrounded by the work pits, each one with its drawing machine. Between the melting end and the neck are the floaters. The five inlets on each side of melting end for combustion air and gas are shown.

molten glass. A fourth kind of brick and shaped slab has been introduced in the construction of glass furnaces, namely, Corhart³ blocks, manufactured by electrical melting of a composition equivalent to that of Mullite, and casting into suitable molds. Corhart blocks^{3a} have a very dense structure and are extremely resistant to the corrosive action of molten glass.

After its construction, the furnace is heated gradually, and it undergoes expansion during this heating. To accommodate this expansion, the roofing arch rests on skew-backs which are carried by horizontal steel beams integral with steel uprights. The distance between the latter is adjustable

³ *Ind. Eng. Chem.*, **23**, 124 (1931).

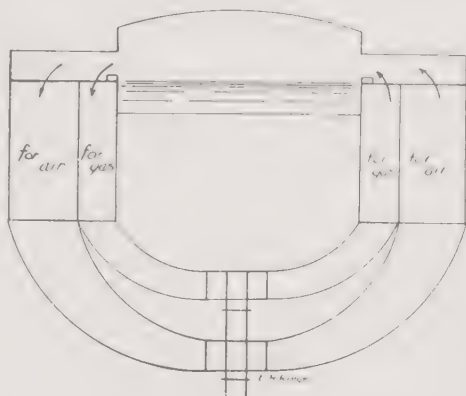
^{3a} The Corhart Standard Electrocast is a cast refractory which is more highly heat- and corrosion-resistant (by melted glass) than any other. It is made by melting in the electric furnace high alumina clays approaching Mullite in composition, and pouring the melt into sand molds, followed by annealing. The Corhart block is too hard to chip or cut; it may be ground on Alundum wheels. In size blocks weighing over a ton are made. For a bulletin, send to Corhart Refractories Company, Louisville, Ky.

by working the nuts on the tie rods which extend the width of the furnace and connect the steel uprights. The nuts are loosened gradually, as the heating progresses.

Once in operation, the furnace never stops; it runs day and night until it has deteriorated so much that it must be rebuilt.

There are five regenerator sets on each side of the melting end of the furnace, each one double, one chamber for air, the other for producer gas. (See Figure 56). The regenerators consist of brick chambers filled with a checker-work of bricks; they are situated on a lower floor, with the inlets to the furnace built onto the side-walls of the furnace proper. When natural gas is used, it is not preheated, but enters directly from the conduit through a flare in the wall of the air inlet, close to the burning space.

FIGURE 56.—The regenerative chambers for air and gas. As shown in sketch, the chambers at the right are giving up their heat; those on the left are storing heat. The chambers are filled with a checker-work of bricks.



When producer gas is used, the gas leaves the producer hot and is prevented from cooling by insulation; it reaches the regenerator bricks (south side, for instance) at 1100° to 1300° F. (600° to 704° C.); the regenerator raises it to 1800° F. (982° C.). The air in the meantime is brought to 2200° F. (1204° C.). Gas and air meet just inside of the furnace, so that the flame forms inward, and sweeps across the width of the furnace, passing out through the regenerators on the other side (north side), which now are brought to a high temperature. After 20 minutes, the direction of the gas and air is reversed; they enter through the regenerators at the north side, sweep across the furnace and now heat the regenerators on the south side. The reversing is done by hand.

There takes place a gradual eating away of the brick at or below the level of the glass, especially near the "dog house." The present remedy is to install a set of water-cooled pipes in contact with the outside of the blocks at the regions of greatest corrosion. These reduce the degree of corrosion; but even with these aids, blocks sometimes are completely eaten away, until the glass itself is in contact with the water coolers. The glass congeals and forms its own retaining wall at those places. Thanks to this innovation, the life of a furnace has been greatly extended. One run of 39 months is on record; a life of 24 months is considered satisfactory, while formerly, 9 months was a long life.

Materials. The materials for making glass are fed in at the "dog house." A batch of 1175 pounds of the mixed raw materials, and 1175 pounds of cullet are introduced every half hour. The batch consists of

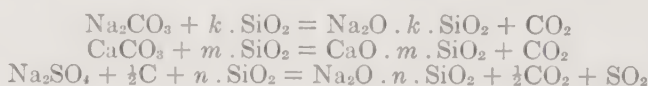
	Parts
Sand	100
Soda ash	30
Lime CaO	16
Salt cake	12
White arsenic	0.5
Powdered cannel coal	0.5

The materials are fed from overhead bins into a mixer suspended on scales, carefully weighed and thoroughly mixed. The cullet (broken glass) comes partly from the plant and partly from outside purchase.

As the materials enter the furnace, they gradually melt, but evolve gas quietly. As one looks into the furnace, the surface is white for a distance of six feet; small pits about 1 inch across may be seen; these are the "rabbit tracks." Further out, there still is much white matter, and a pattern not unlike ribbed sea-sand is visible; these are "gingerbread." A small pool, some 6 or 8 inches across, caused by excess salt cake, which the glass men dread, is called "salt water." One-third of the way down the melting end glass has formed, and whiteness is no longer visible.

Just in front of the floater, the operator watches for a faint line of white bubbles, which should be absent.

The reactions in the furnace probably are:



with $k + m + n$ equaling a little over 5 in this case.

Between reversals of gas and air (*see* Fig. 57), the furnace is absolutely quiet for some thirty seconds, and a view may be had of the glass pool which

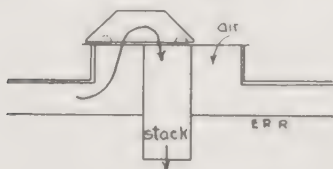


FIGURE 57.—The device for reversing the direction of the flame. A box with open bottom is set as shown, when chambers at the left in Figure 55 are storing heat. After 20 minutes, it is moved to the right, and the inlet for air is then the left passage.

reflects every detail of the roof and sides; so quiet is the pool that it takes a little study to tell where glass ends and exposed wall begins. It is a beautiful sight; a moment more, and the flames have appeared and fill the whole space, cutting off the view.

The hottest part of the furnace is half way down the melting end, 2600° F. (1427° C.); at the floater hole, just in front of the floater, the glass itself is 2430° F. (1332° C.).

The gas consumed per day is 800,000 cubic feet for natural gas. The capacity of the furnace is 1200 tons of molten glass, when the level is carried at 58 inches; one inch in height represents 22 tons of glass. The work pits draw 50 tons of glass a day.

There is a normal shrinkage in the weight of the charge, due to the loss of gases; it is increased further by the volatilization of some alkali oxides. The observed shrinkage is generally 10 per cent (see problem 3). In other words, for 100 pounds of raw materials charged, 90 pounds of glass are drawn from the furnace.

Work Pits. The glass travels through the neck into the refining end, finally reaching the work pits where the drawing machines are situated. The temperature of the glass in the pits is 1860° F. (1016° C.).

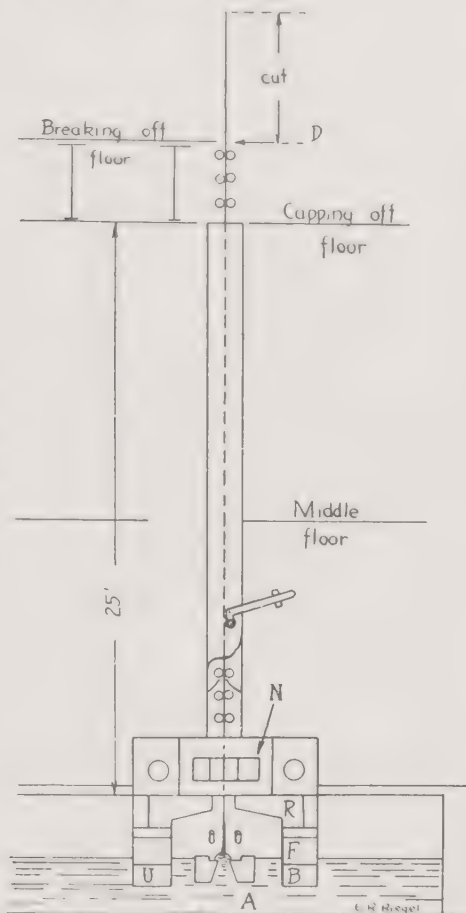


FIGURE 58.—Side elevation of a Fourcault drawing machine. *A*, the débiteuse, clay block with slit; *U* and *B*, under-bridge; *F*, bridge; *N*, annealing box with burners; *D*, level at which diamond line is drawn. The sheet coolers are shown just above the débiteuse.

The essential feature of the Fourcault process is a long rectangular clay piece, with a longitudinal slot, through which the melted glass is "paid out," hence the term, the *débiteuse*. The shape of the *débiteuse* is shown in the elevation of the drawing machine shown in Fig. 58. The clay block floats on the glass, and is forced down a short distance into the glass melt by adjustable arms; its delivery slot is protected by raised edges, so that no glass reaches it from the surface, but a gob is forced up from below. It is this body of glass which is pulled up by the preceding parts of the sheet, to become itself a flat sheet. The action will be clear from Figure 58. The sheet enters the *lehr*, and is pulled up by the asbestos rollers which

bear against it. The rollers on the left side are driven; those on the right are suspended on hinges and free to move outwardly; they bear against the sheet by the weight placed on the outside arm of the hinge.

A flame plays in the heating box and its heat warms the lehr, the temperature gradually decreasing as the distance from the annealing box increases. It reaches the end of the lehr, emerging onto the cutting platform, where it is cut into sheets. A straight line is made by a steel wheel cutter by pulling it across while resting on a light wooden frame which the rising sheet lifts with itself. The lehr is 25 feet high, and the time of annealing varies with the speed of drawing, from 11 minutes for the lightest glass to 45 minutes for the heaviest.

A vane under each of the rollers deflects any broken glass which may drop down the lehr, and ejects it through small swing doors.

The Thickness of the Glass. The same *débiteuse* serves for all thicknesses (called "strengths" in the glass factory) of glass; the strength is controlled by four factors: (1) temperature: the higher it is, the thinner the sheet; (2) depth of block in the melt: the deeper it is, the thicker will the sheet be; (3) sheet coolers: the closer, the thinner the sheet; (4) the speed of draw: the higher the speed, the lower the "strength." The rates of draw are roughly as follows:

	Inches per minute	Width, inches	Annealing time, minutes
For single strength	28	62	12
double strength	18	63	17
heavy strength ($\frac{3}{8}$ inch)	11	65	27
heavy strength ($\frac{1}{2}$ inch)	7	65	45

As the sheet forms, a heavy edge develops and necessitates a recess in the asbestos drawing rolls, as indicated in Figure 59. The edges of the

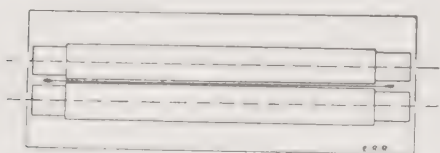


FIGURE 59. — Horizontal cross-section through the Fourcault lehr, showing two asbestos rollers, and the glass sheet with its thickened ends. The rollers are made smaller in diameter at the ends in order to accommodate this extra thickness.

sheet are removed on the cutting floor, by trimming 3 or 4 inches off the sides, and are sold for glass shelvings in small medicine closets, show counters and the like. The cut sheets are placed in a warm dilute hydrochloric acid bath for a short time, to remove sublimed alkali which later would cause dullness.

From the cutting floor, the cut sheets are wheeled to the cutting room where the glass is sorted and defects removed, care always being taken to produce useful sizes. The grades are A, B, and C, defined by one of the government agencies.

The largest sheet made by this process is 120 inches by 60 inches.

General Remarks. A slight change in temperature may throw a furnace out of its stride, and it may be two weeks before it is brought back to correct production. A change in temperature may cause "stones" in the sheet, which make it unsalable. In addition, there may be blisters, seeds, and

waves due to various derangements. The heat of a glass furnace is not watched in order that it may show a nice balance, but the wise operator spends plenty of money for heat in order to insure steady production of the higher grades. It takes very little time to lose the equivalent of a fuel bill in poor glass. The choice of the composition of the glass is of the greatest importance, to indicate the general trend, it may be said that a short period of annealing calls for a softer glass, richer in alkali, than would otherwise be necessary.

THE COLBURN PROCESS

This process depends upon the special machine invented by Colburn⁴ and gradually perfected. This machine consists of a cylindrical roller over which the sheet of plastic glass is bent from its original vertical position to the horizontal position; of a bar which starts the sheet; of small knurled cold rolls which set its edges; of grip bars placed beyond the bend-

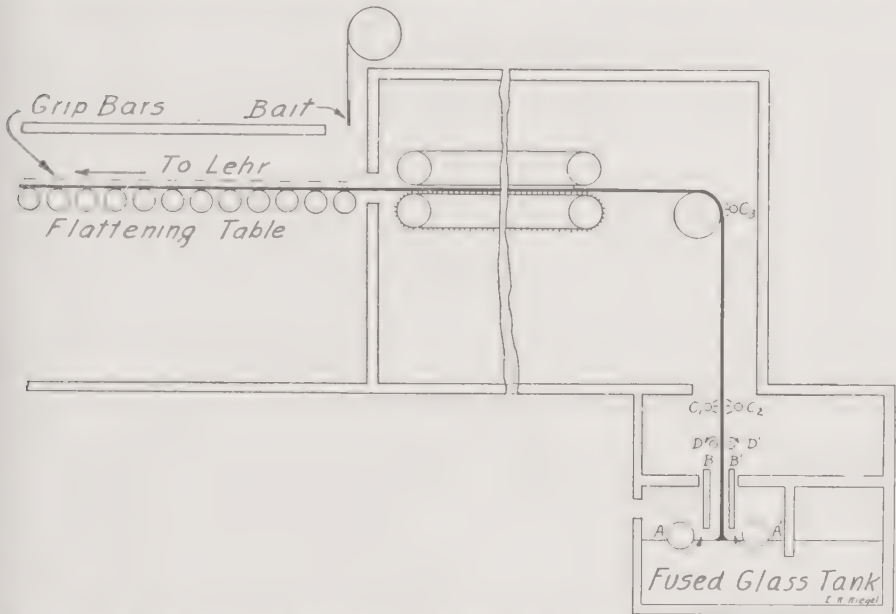


FIGURE 60.—Side elevation of scheme for making window glass by the "flat-glass" system. A, A', rollers of the same width as the sheet which feed the glass to the point of draw; B, B', water-cooled shields which protect the sheet from flames from near-by burners; C₁, C₂, C₃, flames to keep glass from cooling below the plastic stage; D, D', are water-cooled, knurled rolls which form the edge of the sheet and pull on it; there is a pair of such rolls on each edge of the sheet. The edges are formed thicker than the main part of the sheet.

ing roll which pull the sheet along; of a flattening table, and a lehr. In addition, numerous auxiliary devices, each one indispensable, and perfected through trial, are part of the process. Nearly all the essential features are covered by patents.⁵ (See Fig. 60.)

⁴ Frank W. Colburn, whose process, with certain improvements, is now used by the Libbey-Owens Glass Co., Toledo, Ohio. The plants are located at Toledo, O., Shreveport, La., Charleston, W. Va., and Hartford, O., Ottawa, Ill.

⁵ The bending roll, in U. S. Patent 826,439, Claim 21; the bearing belt and grip bars, in U. S. Patent 849,351 and 876,267; the knurled rolls in U. S. Patent 970,182, Claim 2.

The following description of the process is taken from a booklet published by the company using the furnace:

"To start the drawing of the sheet the Colburn machine is placed in reverse motion, which allows a bait to be introduced into the drawing pot containing the molten glass. The bait consists of a flat iron bar 3 inches wide and about 6 feet long, attached to the strips of flexible metal which allow the bait to pass over the bending roll, down into the glass. The molten glass immediately adheres to this bar. Then the machine is placed in forward motion thus pulling the bait with its adhering mass of plastic glass over the bending roll into the flattening table and thence into thelehr. When the bait reaches the end of the flattening table, about ten feet from the bending roll, it is cracked off and removed; and the sheet of glass continues on its way, through the 200-foot annealing lehr.

"During the drawing the sheet is kept at an even width by passing the outer edges of the sheet between two sets of water-cooled knurled rolls placed an inch or two above the surface of the molten glass, just inside the edges of the drawing pot. These knurled rolls engage the sheet for about two inches on each side and serve to sustain it at a constant predetermined width. These edges are thicker than the intervening sheet of glass, and the real pulling of the sheet is accomplished by engaging the outer edges of the sheet—after it has passed over the bending roll—between the flattening table and a series of grip bars running in the same direction and placed just above the flattening table.

"The lehr is provided with two hundred power-driven rolls, covered with asbestos composition, over which the glass passes in continuous sheet form emerging at the end onto a movable cutting table. Here it is cut into sheets of suitable size, dipped in a hot solution of hydrochloric acid and then distributed to the cutting stalls. The sheets are graded and cut into commercial sizes and packed in boxes each containing fifty square feet of glass. This sheet glass is absolutely flat and free from the distortions ordinarily noticed in window glass."⁶

The batch for this process is made up in approximately the following proportions: 100 parts sand, 35 of limestone (CaCO_3), 28 of soda ash, 6 of salt cake and 0.6 of carbon.

The Pennvernion Window Glass Process. In this method of working the sheet is drawn from the glass melt through the slot of a submerged clay block and raised vertically through the lehr, as in the Fourcault process.

Hand-blown Window Glass, and the Machine Cylinder Method. The old way of making window glass was to blow (from the lungs) at the end of an iron blow-tube or pipe, held in the hand, cylinders not over 5 feet long nor over 15 inches in diameter. The glass had to be reheated several times, reblown, and the two ends removed. The cylinder so obtained was cut lengthwise, and allowed to flatten in a furnace similar to the one used in connection with the machine cylinders.

In the machine cylinder method, cylinders 48 feet high and 28 inches

⁶ "Flat Glass," by Arthur E. Fowle, The Libbey-Owens Sheet Glass Co., Toledo, Ohio, published by the company in 1924.

... were drawn upward by mechanical means. The cylinder was cut into short lengths, then halved, and the halves flattened in an auxiliary furnace with a turn table. The process became obsolete, at least in the United States, when patent protection on the Fourcault process came to an end.

Wire Glass. Wire glass is an important structural glass. It is made by laying a steel wire netting into soft glass between two rolls immediately after the glass has been fed from the furnace. The operation may be a continuous one, and a sheet 5 feet wide may be made at the rate of 20 feet a minute; it is cut by bending it in the shape \neg , when the wire breaks easily. (See Fig. 61.)

Figured glass, often called Florentine glass, is made by forming the sheet between two rolls, which may have a design cut on one or both. When the design is a square or a cube which must retain the proper shape to give the desired effect, the sheet may be formed on a table, and a roll bearing the design passed over it.

FIGURE 61.—Apparatus for the continuous drawing of wire glass.
A, the glass furnace, working end; B, sheet of iron wire.

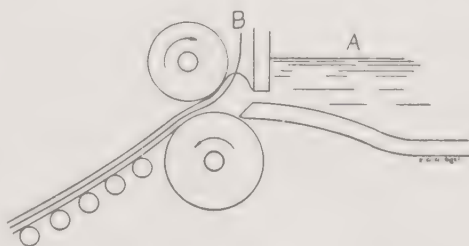


Plate Glass. The composition of plate glass is approximately the same as that of window glass; it is a lime-soda silicate, but is thicker than window glass, for the sake of strength in the finished plate, and also to prevent or reduce breakage in the long process of grinding and polishing which it invariably undergoes. In fact, the distinguishing feature of plate glass is that it is free of distortions, that its surfaces are absolutely true. Attempts to produce a continuous sheet of glass thick enough to have the strength desired in large sections have been successful; the Pittsburgh Plate Glass Company's continuous method produces an endless sheet by feeding the molten glass from a furnace continuously between two water-cooled rollers about 12 inches in diameter. Once formed, the sheet travels through a *lehr*, and is then cut into sections which are ground, polished and washed.

Plate glass by the standard, older process is poured in single sheets. The furnace may be of the continuous type, as for window glass, or pots may be used; the latter case is the more common. The glass from a pot, lifted by mechanical tongs, is poured onto a cast-iron table (built of segments) and leveled by a heated roller. The rough plate is annealed, then set in plaster of paris on a flat table, ground with 5 grades of sand, decreasing in coarseness, then 5 grades of emery,⁷ and polished with rouge.⁷ Both sides of the plate receive this treatment, in the course of which about half the thickness of the glass is lost.

⁷ Emery is the natural crystallized alumina (Al_2O_3); rouge is the oxide of iron obtained by roasting copperas ($\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$).

In the Ford continuous sheet process,⁸ the glass flows from the furnace onto the metal table, and is leveled by passing under two Nichrome cylinders, the second smaller than the first. The glass sheet continues into a Lehr, 500 feet long, where it cools from about 1100° F. (593° C.) at entry to 100° F. (38° C.) at the exit. It is cut into suitable sizes, mounted in plaster of paris, and ground and polished as single plates. The process was developed especially for making the glass parts for the safety glass windshields for Ford automobiles.

The most recent process for high-quality plate glass is that of Bichoux,⁹ in which the melted glass, poured between two rollers, comes out on a moving table, is fed to a Lehr, annealed, and cut into suitable lengths. The grinding and polishing are the same as described above.

Health Glasses. In order to permit the short invisible rays of the sun to reach the inside of dwellings and offices, the glass for the window must be selected for its transparency to such rays. Ordinary window glass stops them by absorption. A window pane of clear quartz glass is transparent to solar ultraviolet rays, but quartz glass is too expensive for general use. Corex, made in several grades, may be a phosphate glass, or it may have a composition similar to that of "Pyrex." The phosphate glass has a transmission practically equal to that of quartz glass, but is not completely resistant to atmospheric moisture. The borosilicate, Corex, transmits much of the solar ultraviolet, and is very resistant to atmospheric attack. Substances other than glass are transparent to the solar (and still shorter) ultraviolet rays, such as Aldur,¹⁰ a urea-formaldehyde condensation product, colorless and transparent in the visible.

The health glasses undergo solarization, that is, when first exposed to the sun, the original transparency to the short rays diminishes by 20 per cent; after this loss, the glass is stabilized, and continues to transmit a constant percentage of solar ultraviolet rays.

The percentage transmission of a number of materials, the range which they transmit, and also, the range of solar short rays, are indicated in Figure 62.¹⁰

Safety Glass. Safety glass, also called laminated plate glass, consists of two sheets of plate glass cemented together by a sheet plastic, forming as transparent a whole as the component parts singly. Such laminated glass may be shot through by a bullet without shattering; it breaks and is pierced, but the segments remain in place. Originally a thin sheet of pyroxylin was used; cellulose acetate plastic, and acrylate resin plastic were successive improvements. Today it is thought that polyvinyl acetate resin, made by treating polyvinyl alcohol with a moderate amount of formaldehyde, with softener and plasticizer, is superior to all other cementing resins; a safety glass containing the polyvinyl acetal resin, after being broken, may be rolled into a bundle without shedding the fragments: the

⁸ "Making glass for Ford windshields," F. J. Huntley, *The Glass Industry* (1923), 4, p. 1; "Continuous process for plate glass at Ford River Rouge plant," E. P. Partridge, *Ind. Eng. Chem.*, 21, 11 (1929).

⁹ Described in "Die Glassfabrikation," Dralle-Keppler, Oldenburg, Verlag Fischer, Vol. 1, 1923, Vol. 2, 1931, which gives the list of patents on this process.

¹⁰ "Ultra-violet transmission of a new window-glass substitute," R. H. Christ, *Ind. Eng. Chem.*, 2, 1367 (1928), and: "Special characteristics of light sources and window materials used in therapy," W. V. Coblentz, *Trans. Illum. Eng. Soc. (N. Y.)*, 23, 247 (1928).

sin stretches. There is also in use a polyvinyl butyrate plastic called i-Test, which will elongate 300 per cent.*

There are two methods of assembling. In the dry method, the glass is coated with an aqueous glue solution containing a preservative, dried, and the cementing sheet placed between two glass plates, sandwich fashion. The assembly is placed in bags, evacuated, then taken out and sealed along the edges. In the wet method, the glass receives a resinous lacquer coating; the cementing sheet receives a coating of bonding solution on both sides; the pieces are assembled, and after evacuating, sealed all around.

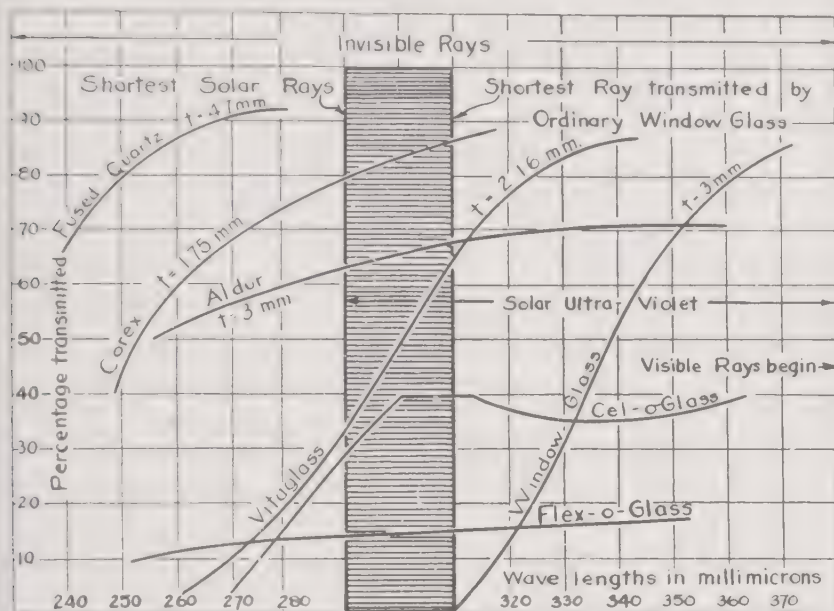


FIGURE 62.—Curves showing the percentage of short light rays transmitted by various glasses and other substances. The thickness is given as "t." The shaded area represents the "vital rays." (See references in text.)

At temperatures below 0°F [-18°C .] safety glass of the older type is no longer safe, while at temperatures above 120°F . [49°C .], there is danger of softening of the pyroxylin film, and again the glass has no longer the quality of "safety." The use of Vinylite resins has been proposed as a remedy, and also a combination of several plastic sheets, such as a pyroxylin sheet with one of methacrylic ester resin.¹¹ The newer resins are satisfactory in this respect.

An entirely different safety glass is quenched glass, a single sheet, but with hard surfaces produced by quenching, and a softer, more elastic interior layer.

Mirrors. The plate glass is cut to size; it is examined for even the slightest blemish, such as a scratch, which would cause an ugly spot in the finished mirror; all blemishes are removed by polishing with rouge. As a

* *Glass Industry*, 20, p. 450 (1939).

¹¹ U. S. Patent 2,032,663. This patent gives the safety range of regular Celluloid-laminated glass 120°F . to 60°F .

rule the sheet is first beveled, next freed from blemishes, and is then ready for the final step, the coating with silver.

Just before silvering, the glass is scrubbed, rinsed with distilled water and flushed with a reducing solution, such as stannous chloride or an organic reducer. Without draining it, the sheet is quickly placed on a cast-iron hollow table top covered with felt, and kept warm by steam in the interior chamber. The glass is leveled by means of wedges and a soft pad under the center, to prevent sagging. A solution of silver nitrate, slightly ammoniacal, is poured on from a pitcher and the sheet left undisturbed for an hour. A lustrous deposit of silver gradually forms. Next the deposit is dried, coated with shellac, and later with paint.

Other procedures include, after thorough cleaning, a preliminary treatment with 0.1 per cent stannous chloride solution for $\frac{1}{2}$ minute, rinsing and application of the mixed silver solution, containing the reducing agent added just before use. This latter agent may be formaldehyde, glucose, Rochelle salt (requires boiling), tartaric acid, and others.

A formula might be: *A*, silver nitrate 10 grams, distilled water 50 cc., ammonia to precipitate and then redissolve the precipitate, enough more water to make 1000 cc.; filter. *B*, silver nitrate 2 grams, dissolve in 10 cc. water, dilute by adding boiling water to make 1000 cc., then add 1.66 gram Rochelle salt and continue boiling for 20 minutes, until nearly clear; filter hot, and cool to room temperature. Equal parts of *A* and *B* are mixed just before using.

The solutions need not be hot; if they are used cold, a harder film is produced. More dilute solutions produce a thinner film, which may even be transparent.¹²

Mirrors are now made also by a spray process, in which the silvering chemicals are applied in spray form.^{12a}

In addition, smaller and special mirrors receive their reflecting coating by the deposition of metal which has been vaporized electrically in vacuum.

Double-walled Dewar flasks are generally silvered, and are known under the trade name of "Thermos."

SPECIAL GLASS

Special glasses are those which serve special purposes, and must possess those properties which make them suitable. They include optical glass, thermal glass, chemical glassware, cut glass, and colored glass. Compared with window glass, the tonnage they represent is insignificant; on the other hand, their price is high.

The materials for the manufacture of optical glass must be purer than for common glass, and the variety is greater. Two properties of glass are chiefly the concern of the optical glass maker, namely, refraction and dispersion.¹³

¹² "On the silvering of glass," by Donald E. Sharp, *Glass, Ind.*, 11, 273 (1930).

^{12a} The Peacock Laboratories, Philadelphia, Pa.; see *Ind. Eng. Chem. (News Edition)*, 18, 199 (1946).

¹³ By "mean dispersion" is meant the difference between the index of refraction for the red line of hydrogen H_{α} and the index for the blue line H_{β} . The difference is not the same for various glasses. The dispersion for any two lines may be studied.

The term *crown glass* means a glass of low refraction and low dispersion, *flint glass* means a glass of high refraction and high dispersion. This rough classification serves well for general purposes. It might be added that crown glass is a lime-soda glass, hence essentially the same composition as window glass; flint glass is a lead-potassium glass. A more accurate division is the following: In the expression

$$v = \frac{\text{refractive index} - 1}{\text{dispersion}}$$

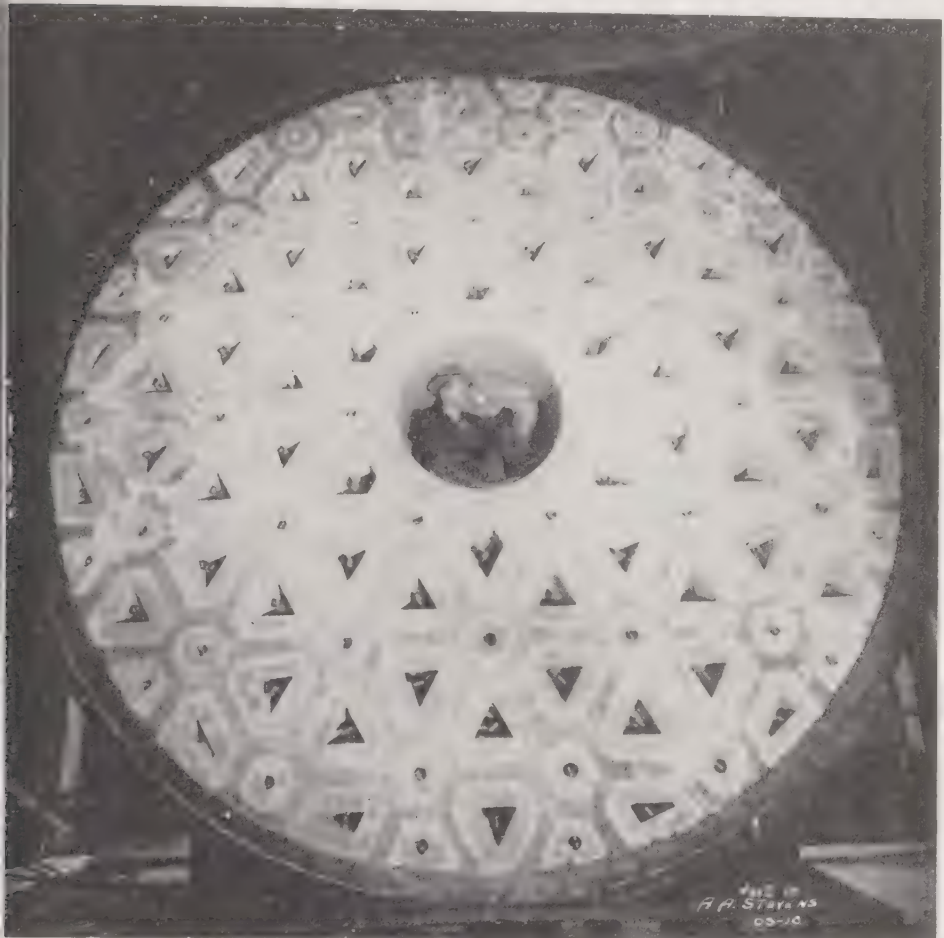


FIGURE 63.—The “Pyrex” Glass telescope disk, 200 inches in diameter, seen from the back side, before the core material was removed. The glass portion may easily be traced because the glass as shown in the photograph is darker than the core material. (By permission of the Corning Glass Company.)

The glasses of the crown glass type have a v value generally over 55; those of the flint glass type have a value below 55.

In addition to the standard optical glasses, new glasses in which rare-earth oxides are combined with boron and sodium have been developed:

these non-silicate glasses have dispersions which are not a function of the index of refraction as in the *silicate glasses*.^{13a}

Optical glass is made in small batches, which are melted in individual pots.¹⁴

Much attention was devoted by the general public to the casting and transporting of a 200-inch diameter "Pyrex" glass reflecting telescope disk cast in Corning, N. Y., and shipped to the observatory in Mount Palomar, California, where it is now being installed. It is the largest disk ever to be cast, is 26 inches thick, and weighs 20 tons; special apparatus had to be constructed. The reflecting surface of the disk is polished, and coated with aluminum. As shown in the picture, a ribbing reinforces the disk properly in order to stiffen it; otherwise, its own weight, when tilted, would cause enough flexing to make some of the measurements valueless.

Cut Glass. Lead glass is used in the manufacture of cut glass because of its brilliancy. Batches vary, but a fairly representative one for the melting of such a glass might be the following:

Sand	1000	parts
Red lead Pb_2O_3	660	"
Pearl ash K_2CO_3	380	"
Saltpeter KNO_3	130	"
White arsenic As_2O_3	10	"

The article is shaped by pressing or blowing, cooled in the annealing furnace, and passes thence to the cutting room. The design is drawn on the glass with a grease pencil, and is then cut in by means of a small metal aluminum wheel and emery; the surface of the cut is next polished with rouge applied on a wooden wheel. True cut glass may be distinguished by its sharp edges; imitation pressed ware lacks these. For cheaper varieties the design is pressed in and just enough cutting and polishing done to give the characteristic edges. The cutting of glass is also combined with etching to good advantage.

In table glassware, ordinarily called *decorated glassware*, a design is traced in pencil, and the lines or areas are then cut with a small abrasi wheel, reproducing in the glass the pencil design. The cut lines are then dull in appearance, similar to poorly frosted glass. The original brilliant surface may be restored by submerging the glasses alternately in a bath of sulfuric acid, containing some hydrofluoric acid, and in warm water.

COLORED GLASS

The expansion of automobile manufacture and the construction of subway ways, added to greater demands for railway and maritime signals, have increased the importance of colored glass. To these utilitarian purposes must be added the uses of colored glass in tableware, and in the construction of colored windows.

The practice in making red automobile tail lights will serve as an example of manufacture for the smaller pieces. A batch of the red glass is prepared in closed pots (Fig. 64); the composition may be, for instance

^{13a} U. S. Patent 2,150,694 and Reissue 21,175 (1939) to G. W. Morey.

¹⁴ Optical glass was treated somewhat more fully in the second edition.

lime, with 1 per cent selenium. The pot is served by two men and a boy; one takes gobs of clear glass from the inner ring in the pot, and presses them in a mold, disconnecting the gob by means of shears from the pipe. The second man operates the die which, with the mold, forms the finished shape. The boy places the shapes on a flat tool and carries them to thelehr. In order to obtain the red with selenium, it is essential that



FIGURE 64.—Closed pot used for small lots of glass of window-glass grade and for colored glass.

A small amount of cadmium sulfide (1 per cent) be added to the raw materials when mixed at the start.

Ruby red may be produced by adding cuprous oxide to a potash-lead glass; on cooling, the glass is practically clear; it must be reheated in order to develop the splendid red color. Gold ruby is made by adding gold chloride to potash-lead glass, cooling and then reheating to develop the fine-red color. In the glasses just given the color is due to the colloidal state of the copper and gold; it is in the study of gold ruby glass that Leigmondy made the observation which has led to the present important knowledge of the colloidal state of matter, namely, that the color was due to highly dispersed particles of gold, visible in the ultramicroscope.

Yellow glass may be made by adding selenium or uranium oxide to soda-lime glass; or by adding 2 per cent cerium oxide and 2 per cent uranium oxide to soda-lime glass, to produce a brilliant light yellow.

The deep blue color of cobalt is well known; it is obtained from cobalt oxide added to soda-lime glass; a greenish-blue is made by adding cupric oxide instead.

Amber glass is obtained by the admixture of a carbonaceous material with sulfur or iron sulfide in a soda-lime batch.

Opal glass may be made by substituting a combination of calcium fluoride and feldspar for part of the ingredients ordinarily used in soda-lime glass. Other fluorine and alumina-containing materials, such as sodium hexafluoride, cryolite and nepheline syenite may be used in place of the fluor spar and feldspar. Black glass can be made by using an excessive amount of pyrolusite and iron oxide.

Green glass owes its color usually to chromium, added as oxide or as chromate.

THERMAL GLASS AND CHEMICAL GLASSWARE

Window glass is used because it admits light into buildings, and because it is cheap. Optical glass is used to refract, disperse, or condense light. Thermal glass owes its economic existence to its low coefficient of expansion; it can be heated rapidly, or cooled suddenly and unevenly without breaking. The best known of such glasses is "Pyrex," which is made into heating dishes, teapots, and laboratory glassware. The breakage of "Pyrex" beakers and flasks is so low and its resistance to chemical reagents so high that it has been universally endorsed, although it is somewhat higher priced than common glassware. Before the war of 1914-18 Jena glass, also a remarkable heat- and shock-resisting glass, was largely used in the United States.

The composition of these two glasses follows:

	SiO ₂	B ₂ O ₃	Na ₂ O	Al ₂ O ₃	As ₂ O ₃ Per cent	K ₂ O	MgO	CaO	Fe ₂ O ₃
"Pyrex".....	80.62	11.90	3.83	2.00	0.66	0.61	0.29	0.22	0.12
Jena	64.58	10.03	7.38	6.28	0.12	0.08	0.10

Vycor. A new form of low-expansion glass consisting essentially of silica has been developed and is marketed under the general name "Vycor" by the Corning Glass Company. A borosilicate glass of special composition is made into the ware and then heat-treated, when it becomes slightly opalescent. By means of mineral acids the metallic oxides and boron compounds are removed (about 36 per cent of the glass), leaving a transparent body containing a multiplicity of pores. On further heat-treating, the pores are closed while the ware shrinks about 20 per cent, and there results an article consisting of 96 per cent silica, highly resistant to thermal shock.^{14a} Some of its properties are listed in Table 21a.

TABLE 21a.—Comparison of physical properties of fused silica and low-expansion glasses.*

Softening point	1442° C. (2628° F.)	819° C. (1506° F.)	1667° C. (3033° F.)
Maximum temperature for long use	900-1000° C. (1652-1832° F.)	500-600° C. (932-1112° F.)	1100° C. (2012° F.)
Specific gravity	2.18	2.23	2.21
Linear expansion coefficient	$7.8-8 \times 10^{-7}$	$32-33 \times 10^{-7}$	$5.5-5.85 \times 10^{-7}$

* *Glass Industry*, 20, 269 (1939).

Glass Tubing. The manufacture of glass tubing is of particular interest to any student of chemistry. Molten glass flows out at one end of a tank furnace over a nozzle-like spout through which compressed air is introduced. The glass is drawn out by a machine and travels a considerable distance; as it travels it is annealed and cooled. When cold enough, it is cut automatically into prescribed lengths. The size of the tubing and the thickness of wall are determined by the viscosity of the glass and by the air pressure. When rods are to be made, the air is shut off. The product of this operation is remarkably uniform as to size and wall thickness.

^{14a} "Shrunk glass resists extreme heat and cold," *Glass Industry*, 20, 269 (1939); U. S. Pat. 2,106,744, Canadian Patent 364,157, British Patent 442,526, to H. P. Hood and M. E. Nordberg. "Recent trends in glass composition," by Donald E. Sharp, *Glass Industry*, April, 1940.

illary tubing, such as is used for thermometers, is drawn in a similar way.

Fused silica from quartz. In addition to glasses made up of compounds of silica, a glass consisting of silica alone is now available in the form of rods, plates, and other shapes. Plates of fused silica of moderate size, suitable for window panes, are also on the market, although at a fairly high price. Silica permits the ultraviolet rays above 185 millimicrons in length to pass through, hence its great value for health.

Fused silica also has the property of expanding only very slightly with heat, so that sudden changes in temperature do not crack it. It is furthermore resistant to all acids except hydrofluoric. For these two reasons it has found application in chemical laboratories and in the industries. A per cent silica glass has already been mentioned.

X-ray Glass. Metallic lead absorbs x-rays. Lead in the form of lead oxide in glass retains that property, so that lead glasses have become of importance as shields for the operators of x-ray tubes.

Lamp chimneys are still made in great quantities; they must be resistant to high heat. A low-alkali, high-silica, and high-boric acid glass was found to have the desired properties.

Bulbs for Mazda and other electric lamps are made automatically by ingenious devices.¹⁵

Light passing through frosted glass is pleasantly diffused; the matt finish which goes by the name of frosted glass is produced by immersion in a bath containing hydrofluoric acid, and saturated with ammonium fluoride, NH_4HF_2 . Etching of a design may be done in the same way, except that parts which are not to be etched are covered with paraffin. Electric light bulbs are etched on the inside, by pouring the solution within the bulb.

Fiberglas. Fiberglas is glass reduced by a mechanical process to a flexible thread or filament. By throwing a thread of glass, pulled from a heated glass rod, over a rapidly revolving drum, the glass is drawn out into fibers resembling wool or silk; such threads are woven into cloth of various kinds which serve useful purposes, comprising an inorganic textile industry. Besides the continuous filament Fiberglas, a staple fiber is produced. One method might be as follows: A stream of glass drawn from the forehearth of a melting furnace is allowed to cool and harden to a wax-like consistency, and is then directed while still hot into a metal layer machine, wherein it is fused by an oxy-acetylene flame and blown by compressed air into fibers collected in a collecting room. (U. S. Pat. 2,175,225). Another method provides a gas blast within the furnace which syphons the molten glass forward to a glass terminus from which it is blown into a collecting chamber (U. S. Pat. 2,156,316). In still another process a stream of fluid glass is allowed to flow downward through an electrically heated platinum nozzle on a rapidly revolving refractory disk.¹⁶ The resulting centrifugation

¹⁵ *Chem. Met. Eng.*, **39**, 310 (1932).

¹⁶ "The manufacturing, processing, and use of glass fibers," by G. V. Pazsiozky, translated from *tech. Ber.*, June, 1936, by Dr. Samuel R. Scholes, *The Glass Industry*, **18**, 17 (1937) [11 W. 42, New York].

produces threads that are long and short, twisted together, so that product has been designated as "glass wadding."

For staple fiber in general, the length averages 10-12 inches, the diameter in the latest procedures being 0.007 millimeter (0.00028 inch). The continuous fiber is made as thin as 0.005 millimeter (0.00022 inch).

In the form of a felted mass, Fiberglas has become an excellent thermal insulator, almost standard in house and warship construction. Its thermal coefficient is low, 0.266 B. t. u. per square foot area per inch thickness per hour per degree F.¹⁷

A new and promising form of insulating material consists of glass bubbles or shapes filled with cellulose so that it has a sponge-like appearance; it is extremely light in weight. It is made by the addition of selected powdered coals or carbons to melted glass. The cellular glass is black in color.

Silica aerogel has been in commercial use as an insulating material for some time.^{17a}

Glass in neon and in fluorescent lights and signs is described in Chapter 19.

GLASS CONTAINERS

Containers were formerly made by hand; a worker could produce about 300 bottles a day. This is still done for special shapes, and when comparatively small numbers are required. In such cases, the worker works from a "closed" pot, and with an iron blow-pipe, the blow being applied from the lungs. For quantity production of standard shapes, automatic bottle blowing machines have been perfected which produce over 6000 bottles in eight hours. Containers are being made with less glass, and to retain the same strength, the shape has been redesigned (compare the new milk bottle in many localities).

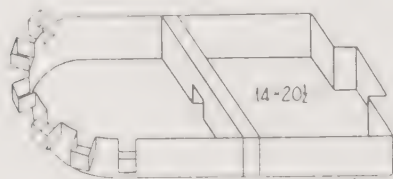


FIGURE 65.—Glass furnace for bottle glass, feeding automatic glass blowing machines. Each of the 6 extensions shown has a machine fed from it.

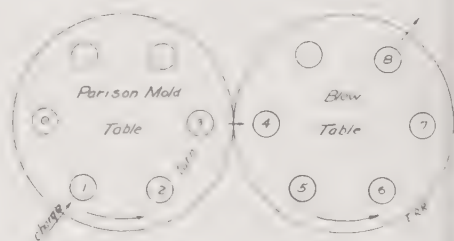


FIGURE 66.—Automatic glass bottle-making machine: the two revolving tables.

In a model American plant which produces a blue bottle for a popular pharmaceutical, the furnace (Fig. 65) furnishes 27 tons of glass a day. The charge consists of 1000 lbs. sand, 380 lbs. soda ash, 100 lbs. feldspar, 140 lbs. lime (CaO), 800 lbs. cullet; for these 2420 lbs., 1 lb. of cobalt oxide (CoO) furnishes the attractive blue shade. A recent major improvement in construction is the triangular doghouse which, with especially designed

¹⁷ "The characteristics of fibrous glass," a booklet which can be obtained from the Corning Glass Co., Corning, N. Y.

^{17a} "Manufacture of silica aerogel," by John F. White, *Trans. Am. Inst. Chem. Eng.*, 39, (presented at the Boston meeting).

charging feeders, permits the automatic distribution of islands of batch to the furnace according to a predetermined pattern; this gives better quality of product and greater yield per furnace.¹⁷ The furnace is fired with oil (72 gallons of oil per ton of glass). From the melting end, the glass passes to the refining end, with 6 extensions, in each of which a clay rod moves up and down, discharging a gob of glass which is cut off by mechanical

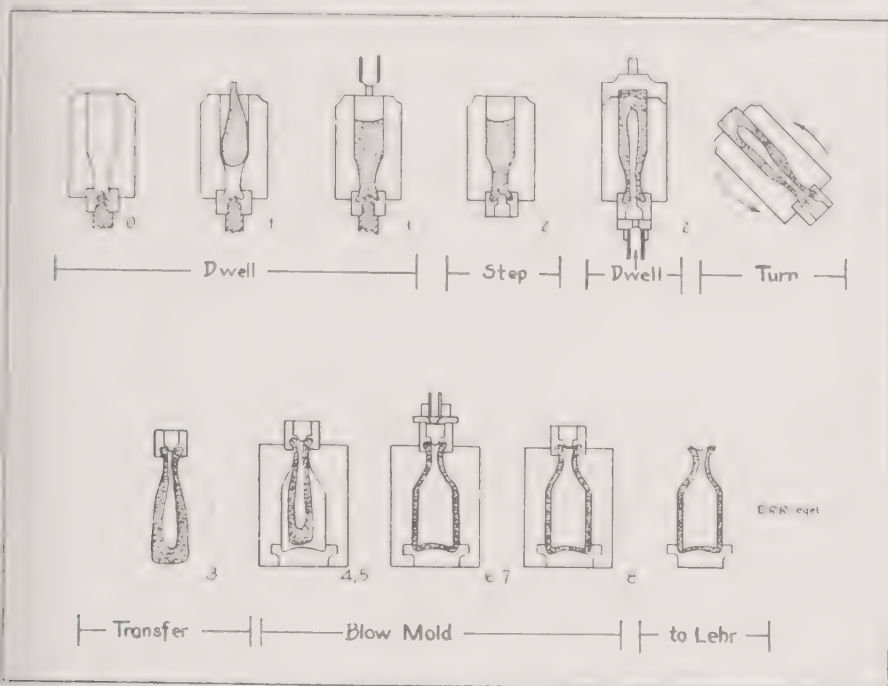


FIGURE 67.—The successive steps in the automatic blowing of a glass bottle. Upper row, the parison mold with its charge; lower row, the blow mold, with charge. No. 3 is the parison. 1. Parison mold arrives empty. Neck plunger comes up. Charged. Compacted by pressure from the top; this forms the finish and gives the neck its final outside diameter and shape (upper half inch of finished bottle). 2. Step to position 2. Counter blow head comes up. Baffle plate comes down. Air blow through neck forms the cavity. 3 and 4. Transfer station. The mold turns between stations 2 and 3. At three, mold halves open, neck mold remains closed. Mechanical arm moves the parison by the neck piece to 4. Here, bottom piece comes up, blow mold closes. 5. Reheating time, that is, a fraction of a second is allowed for heat to flow from the inner part of the glass to the outside chilled layer. 6. First final blow. 7. Second final blow, stronger. 8. Take out. Final step, to Lehr; mold cooling.

scissors. The gob drops into a funnel which guides it to the parison mold marked 1 in Figure 66, which shows the two revolving tables of the bottle-blowing machine.¹⁸ This figure with Figure 67 will make clear the operation of the machine.

The charging of the furnace is continuous, so that the level of the

Mr. "Hartford develops new system of glass melting," *Glass Industry*, February, 1941, with a chart giving typical settings of the timing dials.

¹⁸ For a more detailed description of automatic bottle-blowing machines, see "Textbook of Glass Technology," I. W. Heikin and A. Cosen, London, Constable & Co., Ltd. 1925. New York, Van Nostrand Co.

glass melt is strictly stationary, insuring regular feed to the blowing machines.

The discharge from the blowing machine is onto a conveyor, from which a mechanical arm picks up the bottles one by one and places them, spaced irregularly, onto a moving platform which travels through the lehr for annealing period. The rate of production is 1 bottle in 4 seconds, 900 per hour, for each machine.

Any ordinary bottle shows a thick zone two-thirds of the way down marking where the parison ended. A line just under the neck marks the mold for the "finish." There are two lines up and down on each side. The first marks the halves of the parison; the other, the halves of the blow mold. A line near the bottom marks the blow piece at step 4.

GLASS CONSTRUCTION BLOCK AND ARCHITECTURAL GLASS

For several years, the popular demand for transparent walls has stimulated engineers; as a result of their endeavors there is available today a glass block construction unit, of which one example, a "Pyrex" block measuring $11\frac{3}{4}'' \times 11\frac{3}{4}'' \times 4''$ is shown in Figure 68. The block is a hollow

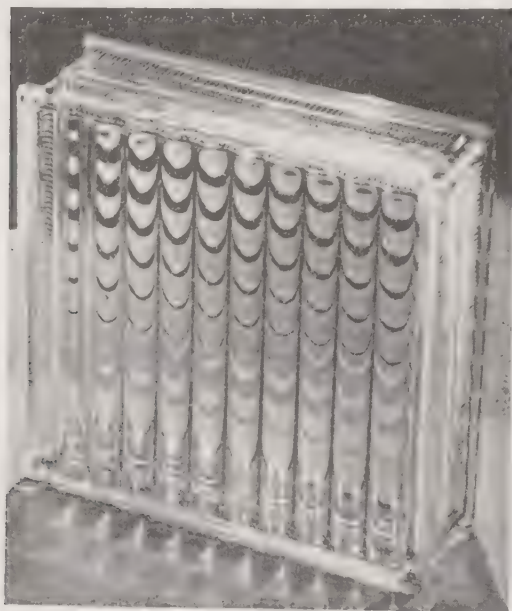


FIGURE 68.—A "Pyrex" construction unit, consisting of a closed cell containing air at reduced pressure, and shown as it would appear from inside a room; manufactured by the Corning Glass Works, Architectural Division, Corning, N. Y.

made of two halves which are fused together hot, so that the interior is essentially dehydrated, and under a partial vacuum. There are indentations on the sides which are to receive the cement with which the blocks are made into a solid wall, or section of a wall. There are now in every example of business buildings and of dwellings in which such "daylight walls" are used. The glass blocks are made by at least two large manufacturers, in a number of sizes, and with a variety of markings. In a block recently introduced, a Fiberglas screen is sealed between the halves into an all glass welded unit; a soft diffused light is produced, with

duces the glare of the sun. Of recent origin also is an aluminized glass which is made by applying a light spattering of molten aluminum from a spray pistol onto the inner part of the two halves of the block, before joining them.

At the same time, the highly decorative effects of molded and shaped glass has led to the manufacture of architectural grilles (such as shown in fig. 69) and panels of great beauty.



FIGURE 69.—A lighting and ventilating grille of "Pyrex," to illustrate Corning-Steuben architectural glass.

As a material for construction for the chemical engineer, "Pyrex" and similar glasses in the form of piping, cylinders, plates, and fractionating towers are now indispensable.¹⁰

TABLE 22.—Selected items in the manufactures of glass and glass products.
(Bureau of the Census)

	1939	1937	1935
Window glass	474,886,321 sq. ft. \$24,326,040	616,566,127 sq. ft. \$31,389,468	428,938,357 sq. ft. \$18,180,053
Plate glass	177,263,478 \$41,818,918
White glass mainly, with others ¹	\$42,532,677	\$62,864,016
Other glass	16,197,002 \$2,291,800	21,343,221 \$2,719,192	11,960,829 \$1,369,144
Sealed glass	21,917,072 \$2,235,080	27,698,404 \$3,966,005	14,372,434 \$1,644,356
Total flat glass	\$71,385,597	\$100,938,681	\$68,266,602
Laminated glass (safety glass)	\$40,395,225	\$76,504,803	\$53,282,938
Mirrors	\$19,127,312	\$19,473,877	\$13,797,368
Glass containers	\$156,364,837	\$162,206,674	\$124,492,570
Glassware	\$2,939,834	\$3,200,840	\$2,759,643
Decorated glassware	\$2,508,334	\$3,343,737	\$1,764,205

¹ Other safety glass, not laminated; rough plate glass, optical glass.

¹⁰ See "Pyrex" liner in ammonia converter in Chapter 6; and compare item in Chapter 45.

OTHER PATENTS

U. S. Patent 1,880,540, electric furnace for melting glass and new type of elect. for such a furnace; 1,920,366, drawing thermometer tubing; 1,838,162, apparatus producing glass tubing; 2,064,361, spectacle glass composition to give a faint shade; 2,056,627, ultraviolet transmitting glass; 1,852,218, apparatus for feeding m. glass; 2,005,194, feeding glass by alternate application of pressure and vac. 1,999,562, continuous production of "plate" glass with one rough and one fire-pol surface; 2,012,583, method of manufacturing bottles; 2,030,810, glass forming and cring machine; 2,045,716, apparatus for casting large telescope disks; 2,053,902, fu for melting glass; 1,981,636, making lamp bulbs from tubing; 2,034,925, hollow building blocks; 1,788,312 and 2,069,130, on glass blowing machines; 1,970,354, on n for feeding glass to the blowing machine; 2,176,654, improved type of glass wall struction; 2,176,012, a vacuum bottle; 2,091,691, on glass compositions.

PROBLEMS

1. Compute the total number of square feet of floor area in the furnace described in the text, with the melting end 52 feet by 26 feet included. Where dimension missing, scale the drawing, for it is made to scale. Each one inch of height of is equivalent to 21.5 tons of glass. What is the apparent specific gravity of the melt from this relation? What is the total capacity of the furnace, to a height of 62 inches?

2. If 60 tons of glass per 24 hours are drawn from the furnace described in Problem 1, how long does any one pound of glass spend in the furnace?

Note: This estimate should be made first on the basis of the calculated capacity in order to indicate the magnitude of the movement. In reality, only the upper 10 to 16 inches of the melt moves and it is this layer which furnishes glass for daily withdrawal, so that the rate of movement is faster than first computed. Make other estimates on movement of 10-inch layer, then 16-inch. The higher the temperature, the deeper the layer which moves. The lower immovable portion is colder and hence more viscous.

3. The materials charged into the furnace every half hour are given in the text. The shrinkage due to loss of CO_2 and SO_2 , calculated on the basis of pure materials would be how much? Express in terms of percentage of the total charge.

If your calculated shrinkage is less than 10 per cent, which is the usually observed shrinkage, the difference might be explained on the loss of moisture, alkali oxides, or other volatile impurities.

4. What will be the molecular formula of the glass? (Divide parts by weight, find the molecular weight of the oxide, tabulate quotients, and divide by the smallest.)

5. Examine a number of bottles for the telltale lines indicating the steps in the automatic blowing operation as described in the text.

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The industrialist deals not only with raw materials and products of reactions, but also with fuels, steam, and electrical power; frequently it is cost of these rather than of raw materials or investment which determines whether a certain enterprise shall be continued or given up. Hydroelectric power and steam-generated power supplement each other. Unlike steam power, hydroelectric power does not reduce our finite store of coal, where it possesses an advantage; on the other hand, if the hydro plant is at so distance from the center of consumption, its performance suffers through loss in transportation of even high-tension current over distances of no more than 100 or 200 miles, so that in this respect, the locally erected steam power plant has an advantage.

Chapter 12

Fuels, Steam Boilers, Hydroelectric Power, Steam Power, and Production of Cold

There are only a few industrial chemical processes in which fuel is unnecessary; an example would be sulfuric acid manufacture. By far the greater number of processes require fuel, or heat produced by resistance to an electric current. High temperatures, in the neighborhood of 1000° are reached by the direct application of fuel, as in the reverberatory furnace.¹ More moderate temperatures, about 100° C., are conveniently reached and maintained by means of steam in jackets, in coils, or led directly into the reacting mixture (wet steam). Soft coal is the important solid fuel at present; the term includes bituminous and semi-bituminous coal. Anthracite² has only slight importance for the chemical and allied industries; soft coal is more abundant,³ cheaper, and in many cases is preferred because of its long flame. For the manufacture of coal gas, only bituminous or semi-bituminous coal is used; if it is of the coking variety, there is left in the retort another valuable semi-manufactured fuel, coke.⁴ This is the most suitable fuel for iron blast furnaces and similar processes, for its hardness and strength permit it to carry great loads without being crushed. Pulverized soft coal burns like a gas. Liquid fuel is chiefly "fuel oil"⁵; it is burned under boilers, in furnaces of all kinds, and to a smaller extent in Diesel engines,⁶ internally. Gasoline⁵ is a specialized fuel, used for internal combustion motors. The gaseous fuels⁷ besides coal gas are natural gas, water gas, butane, propane, and producer gas; for the production of the latter, lignite⁸ may be substituted for the soft coal usually used.

A comparison of the heat value⁹ of the several fuels is given in Table 2.

¹ Compare introduction to Chapter 17.

² The one important anthracite area in the United States is northeastern Pennsylvania (Scranton, Wilkes-Barre, Mauch Chunk).

³ There are about 400 anthracite mines and 9000 soft-coal mines in the United States.

⁴ Chapter 14.

⁵ Chapter 24.

⁶ The Diesel engine has no spark plug; ignition temperature is reached by compression (500 pounds per square inch).

⁷ Chapter 15.

⁸ Lignite contains water; the extensive deposits in the West will probably not be worked intensively until coal is exhausted, except for local needs. North Dakota lignite is being mined now (1937) and utilized for making gas and briquet fuel.

⁹ British thermal unit, the heat required to raise 1 pound of water 1° F.; it takes 4 B.t.u. to equal 1 large Calorie, the heat required to raise one kilogram of water 1° C. (at 18° C.).

TABLE 23.—Comparison of heat values of various fuels.

Anthracite, fixed carbon about 87 per cent	per pound	13,500 B.t.u.
Bituminous coal, fixed carbon about 80 per cent	" "	14,400 "
Coke, fixed carbon about 92 per cent	" "	12,900 "
Wood, dried	" "	8,000 "
Charcoal	" "	12,800 "
Fuel oil	" "	18,500 "
Kerosene	" "	20,000 "
Natural gas	per cubic foot	1,100 "
Coal gas	" " "	600 "

It is evident from this table that bituminous coal is a high-grade fuel, occurs in almost limitless quantities in the United States; a recent estimate is three and a half trillion tons, counting all types of coal. The deposits in England¹⁰ are next in importance; then come France, Russia, Germany, and Belgium. Within the United States, western Pennsylvania and West Virginia lead¹¹; other eastern and southern States with important outputs are Virginia, Maryland, Tennessee, Alabama. In the middle west, Ohio, Illinois, Indiana, Iowa, Missouri, and North Dakota have important coal resources; farther west, Wyoming, Colorado, Utah, New Mexico, Oklahoma and Washington. Coal is generally agreed to be of vegetable origin.¹²

The methods of mining differ greatly. In the Pittsburgh district, there is a five-foot seam near the surface, so that no shaft is necessary, but merely inclined tunnels. This is mined in the following way: "Rooms," 250 feet deep and 20 feet wide, are marked out and the coal removed, leaving a wall between the chambers; a coal pillar must also be left around any oil-well casing reaching to the oil-bearing strata underneath. Within the "room" the cutting of the coal is done by electrical machinery and dynamite. The latter, a low steel truck carrying two motors, travels on narrow-gauge tracks along the tunnels to the room ready for a cut; within the room, it is hauled on rollers, pulling itself by means of a steel cable, drum-wound, looped around a temporary brace jammed between the ceiling (the height of the room is the height of the seam, 5 feet) and the floor. The cutter has a 9- or 10-foot tongue close to the floor; an endless chain carrying short, stout knives travels along its edges, actuated by a sprocket wheel driven by the motor. Power is taken by a flexible drum-wound cable from the copper lead in the tunnel. The tongue is allowed to penetrate into the wall close to the ground, cutting away the coal. The fine coal is swept out by the knives; during this operation, the cutter is hauled close to the wall by the cable, and this pressure forces the knived belt of the tongue inward. With the tongue all the way in, the belt continues running, and the cutter is slowly moved, again

¹⁰ The British coal fields are: *a*. The southern fields, including South Wales and Monmouth, partly under the sea; the coal is of all varieties, bituminous, anthracite, and intermediate; the seams are only over 3 feet in thickness, usually less. *b*. The central fields, North Wales, Yorkshire, Derbyshire, Lancashire, and the Pennines; the coal is of all varieties, bituminous, anthracite, and intermediate. *c*. The northern fields, Scotland, Durham, which give good coking coal. The Ruhr district gives mainly coking bituminous. The basin in Northern France adjoins and in fact is part of the Belgian field; the coal is bituminous of all varieties. The Saar Valley coal is non-coking.

¹¹ Production in millions of tons in 1940 (Minerals Yearbook): W. Va., 126.3; Pa., 112.9; Ill., 49.5; N. Y., 48.4; O., 22.1; Ind., 18.6; Va., 14.95; Ala., 15.15; Kansas-Mo., 6.7; Col., 6.5; Tenn., 6.0; Ky., 5.7; Iowa, 2.9; Total bitum. coal, 453,245. Penn. anthracite, 51,485.

¹² The very interesting and rather satisfactory theory that coal is a petrified residue of prehistoric plants of various kinds, rich in oily matter, sugar, starch and albumen, has been advanced recently. It not only would stand in the same relation to ours as the dinosaurs to our present-day animals. Amber is an example of petrified gum, whose history we know. Private publication by Dr. Samuel Braum, Prague, Czechoslovakia, 1926. Petroleum had its origin, in this theoretical consideration, in the oil enclosed olives the size of melons, which flowed into cavities in the earth's crust; by later geologic events, these chambers were sealed.

by its own cable, from one side of the room to the other, clearing a horizontal space 6 inches high, 9 feet deep, and 20 feet wide. The cutter is removed from the room by its two operators, and the miner takes charge. Two or more holes are drilled into the coal, 5 feet deep, and set close to ceiling; they are filled with dynamite and fired. In nearly every case the whole block, 5 feet by 6 feet by 25 feet, is tumbled down.¹³ The mi-

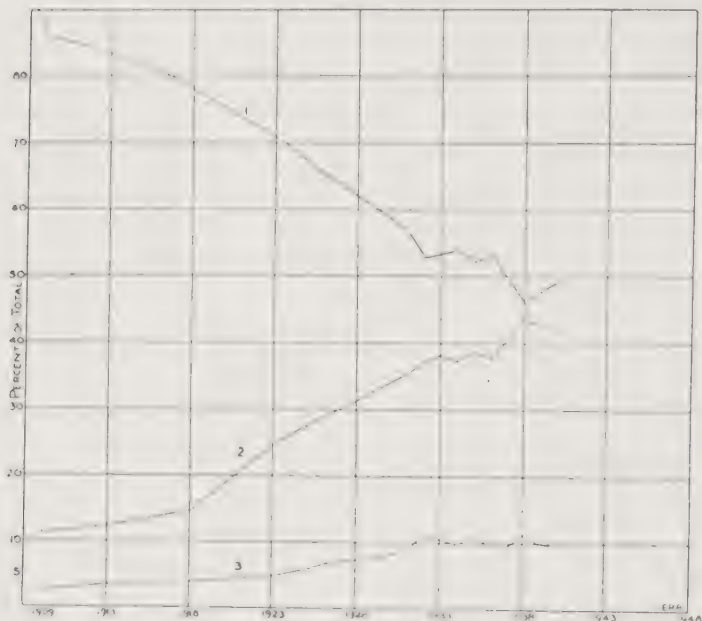


FIGURE 70.—Curves showing the relative importance of the several sources of energy over a period of years. Curve 1, coal; 2, petroleum oil; 3, natural gas; 4, water power. 3. The sharp drop in coal and the equally sharp rise in oil and gas is well shown, to 1932; since then, the lines are roughly parallel. The water power is converted into its equivalent by adding a unit consumption of 4 pounds of coal for each kilowatt hour. (Figures from Bureau of Mines Coal Economics Division and Minerals Yearbook.)

with his helper loads the coal on the low mine cars and these are pulled by an electric locomotive, at high speed, to the breaker house or tippie where the coal is crushed somewhat, freed from fines, and loaded by gravity (the breaker house is elevated) into railway cars.¹⁴ The loading of the mine cars is increasingly mechanical by means of portable belt conveyors or conveyor with reciprocating motion.

TABLE 24.—Distribution of the bituminous coal consumed domestically in 1940. (Minerals Yearbook, 1940)

Coal fed to beehive coke ovens	4,803,000 tons
Coal fed to by-product coke ovens	76,583,000 tons
Coal for locomotive fuel	78,966,000 tons
Coal used by electric power utilities	53,398,000 tons
Coal for general manufacturing and other uses	212,307,000 tons
Coal exported	430,724,000 tons
	16,466,000 tons

For household use, anthracite is preferred to soft coal,^{14a} at least in the areas not too far from western Pennsylvania. Its use has been made mo-

¹³ The lay-out of the room is so planned with reference to the structure of the coal that the miner finds the lines of weakness, and as a result the coal falls forward with minimum blasting.

¹⁴ The Primrose Mine, Carnegie Coal Company, Pittsburgh, Pa.

^{14a} In North Dakota, which possesses no other fuel than lignite, this low-grade material is mined, distilled in special patented retorts, furnishing gas to municipalities, and briquet fuel to the state and to neighboring states. The development of by-products is under intensive study. There were produced in the United States (1939) 3 million tons of lignite, of which 2.1 were mined in North Dakota, 0.8 in Texas, and the rest in South Dakota and Montana; the average value was \$1.13 (Minerals Yearbook).

attractive by the application of a spray of calcium chloride solution, which prevents the formation of dust.

"Blue coal" is anthracite sprayed with a suspension of finely divided ultramarine or "Celestial Blue" in water, followed by partial or complete drying.¹⁵

The distillation of coal is described in Chapter 14; its hydrogenation, in Chapter 24.

STEAM BOILERS

Stationary boilers fall into two classes: water-tube boilers, in which the water is inside the tubes, the fire gases on the outside; and fire-tube boilers, in which the fire gases pass inside the tubes, while the water is on the outside. Both types have one main drum or several drums which carry the greater part of the water. Locomotive boilers are fire-tube boilers; marine boilers of the older types are fire-tube boilers also, but the greater portion of the newer marine boilers are water-tube.^{15a}

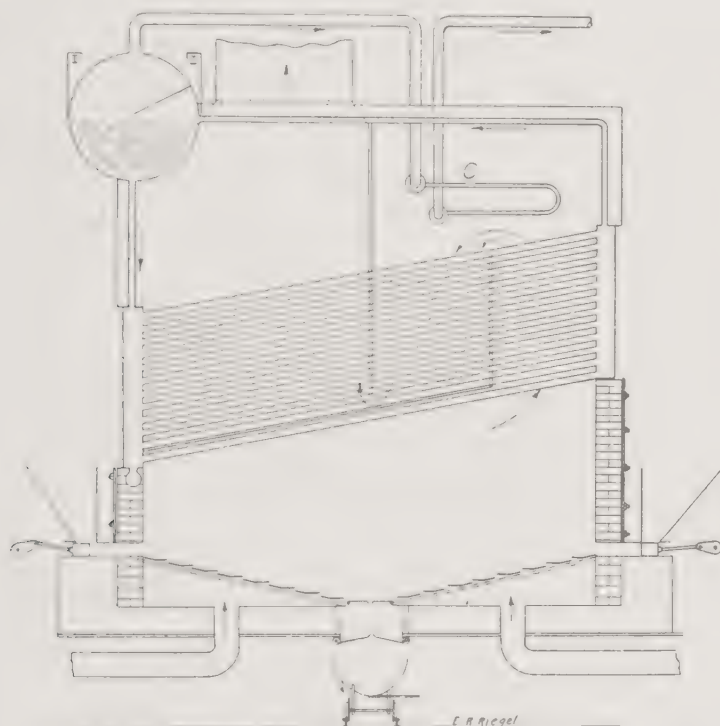


FIGURE 71.—A water-tube boiler, with superheater at C. The circulation of the water and steam is shown, also the entry for the forced draft under the grate, the method of removing ashes, and the travel of the fire gases.

Water-tube boilers are more efficient and safer; they are used for medium pressures, such as 200 and 275 lbs. steam pressure per square inch, as well as for higher pressures, up to and even over 1,800 lbs. per square inch, as

¹⁵ U. S. Patent 1,688,695, to Dr. Gustavus J. Esselen; no adhesive is required.

^{15a} *Complete Marine Age* for December 1941, "A 1200-pound reheat marine installation," by Benjamin Fox and Richard H. Tingey, with discussion by W. W. Smith.

will be discussed more fully later. Their development is more recent than that of the fire-tube boilers. The Babcock and Wilcox, the Stirling, and Heine boilers are water-tube. In Fig. 71, it may be observed that the gases strike the tubes at right angles; while in fire-tube boilers, the path of the fire gases is parallel to the tubes. The exchange of heat is more rapid with the former construction. An illustration of the fire-tube boiler is given (Fig. 72); it is cheaper in first cost, well suited to smaller plants, particularly for pressures of the order of 60 lbs. per square inch.¹⁶ Both illustrations furnish a number of details. Vertical tube boilers, which may be of the transportable type, have fire tubes.

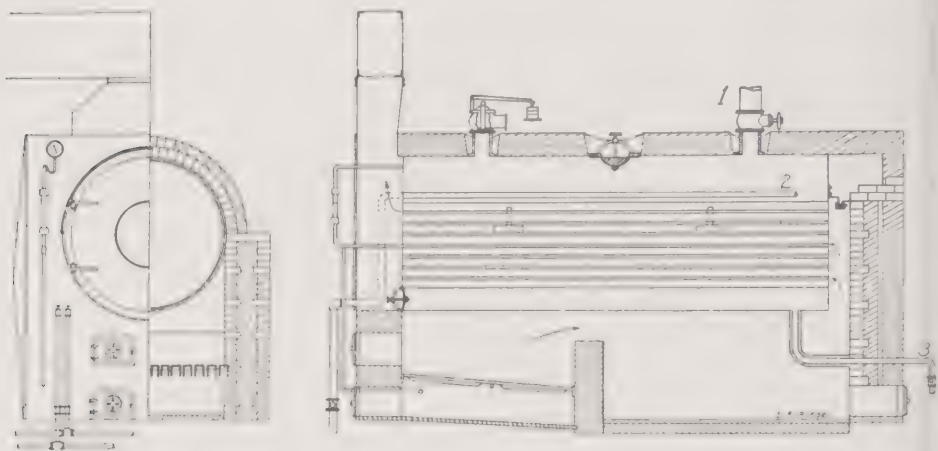


FIGURE 72.—A fire-tube boiler, with hand-fired grate and natural draft; the steam leaves at 1; the feed water is delivered at 2; the blow-off cock is 3.

The material for the drums is mild steel, usually one-half inch in thickness, riveted; the tubes are rolled or spread to fit. In the superheater shown in the water-tube boiler sketch, the steam, after it has left the boiler system proper, is passed through a nest of pipes placed in the flue gases, where its temperature is raised 100 or more degrees above the boiler steam temperature. This treatment raises the work value of the steam, and is important for steam used in engines and turbines; for steam used for heating coils and jackets, such as the chemical engineer requires, it is less important for it does not raise the heat value of the steam by very much.¹⁷ For this reason it is common practice, in chemical plants having medium-pressure steam, to use superheated steam in a single-stage engine working for example between 275 and 40 lbs., and to use the exhaust steam for heating. In general, exhaust steam from pumps, engines, and compressors is collected in steam drums and fed from there to heating coils, sending fresh steam from the boiler into the drum only when the supply of exhaust steam is insufficient.¹⁸

¹⁶ If the steam must travel a long distance (2000 feet for instance), high-pressure steam is preferred, for smaller pipes will transport the same amount as larger pipes carrying low-pressure steam.

¹⁷ Sixty-pound saturated steam has a heat content of 1177 B.t.u. per pound of steam; 60-lb. steam with 100° F. superheat has a heat content of 1227 B.t.u. The temperature of steam rises with rise in pressure; 60-lb. steam is 293° F.; 100-lb. steam 328° F.; 200-lb. steam 382° F.; the pressures are absolute. Marks, "Mechanical Engineers' Handbook," New York, McGraw-Hill Book Co.

¹⁸ The regulation is by means of a Locke damper or other regulator.

Two steam boiler installations for chemical plants, both possessing a high degree of economy of operation and reliability for continuity, have been described in the literature, with illustrations.¹⁹ In one plant, it had been found that autoclaves could use profitably steam at 250 lbs., while other processes needed steam at 125 lbs., and still others steam at 40 lbs.; the plant was to generate its own electric power. There were installed three boilers generating 260,000 lbs. of steam per hour, at 250 lbs. pressure, 406° F. (208° C.) for the saturated steam, provided with oil or pulverized coal firing interchangeably. Two 3500-kilowatt turbine generators were installed, and 40- and 125-lb. steam drawn off from their casings. In the other installations, a boiler generating 488-lb. steam was installed and run to give 400-lb. steam, whose temperature was raised to the required 250° F. (383° C.) by means of superheaters. The steam was applied to a turbine for power generation; the turbine delivered on its low-pressure side the 125-lb. steam which was required for the processes.^{19a}

For the development of high temperatures, diphenyl boilers, or diphenyl oxide boilers are in use. With a pressure of 144 lbs. per square inch (gauge pressure), a temperature of 750° F. (399° C.) is attained. The pressure is moderate, and the temperature may be maintained constant without any difficulty.

High-pressure steam boilers with high-temperature steam are discussed later in this chapter.

All steam boilers are now rated in terms of the pounds of steam generated per hour.

Water Softening. To prevent or at least minimize scale formation, the water fed to the boiler must be freed from dissolved calcium and magnesium salts. For water with carbonate hardness, containing calcium carbonate held in solution by carbon dioxide, milk of lime may be added, which will cause the calcium carbonate to precipitate. For water with non-carbonate hardness, containing calcium sulfate, soda ash is used. The treatment is best performed in separate vessels, and the water filtered by percolation through sand; or the softening chemical is sent directly into the boilers. In either case, the boiler must be blown once or twice a day, for the soluble salts accumulate, and such solutions cause "priming" and other difficulties. By opening the blow-off cock, shown in Figure 72, a portion of the contents is removed and replaced by cleaner water. The task of supplying clean water to the boiler is lightened by returning all clean condensed steam to the boiler room. The boiler feed water is generally preheated.

Recent work in the Bureau of Mines has led to the recommendation that trisodium phosphate be used for conditioning boiler water. The muds formed are more soluble, or as soluble, in very hot water and therefore do

¹⁹ "Cheaper power for the chemical industry," W. S. Johnston, *Ind. Eng. Chem.*, 23, 476 (1931).
^{19a} A variety of boilers is available, for example: A controlled radiant steam boiler with pulverized fuel system, 1,000,000 lbs. of steam per hour capacity, at a pressure of 1,800 lbs., with steam temperature 545° F.; a type VM boiler with coal stoker, capacity 23,000 lbs. per hour, steam pressure 275 lbs.; type VA boiler, with multiple retort stoker, capacity 90,000 lbs. per hour, pressure 200 lbs., steam temperature 271° F.; type VI-Z boiler, with spreader stoker, capacity 38,800 lbs. per hour, pressure 275 lbs., steam temperature 505° F.; type VE boiler, traveling grate stoker, capacity 185,000 lbs. of steam per hour, pressure 1425 lbs., steam temperature 930° F.; VU steam generator, C-E pulverized fuel system, capacity 70,000 lbs. of steam per hour, pressure 450 lbs., steam temperature 625° F.; premier boiler with water stoker, capacity 1000 lbs. per hour. (From a list from Combustion Engineering Company, Inc., 40 Madison Avenue, New York.)

not form a scale, but float so that they can be removed by a special filter installation. It has been shown in the course of this work that soda solutions tend to render steel brittle.

Carbonate hardness may also be removed by heating in a vessel with trays, having provision for the escape of the carbon dioxide driven out. The calcium carbonate precipitates on the trays, which are removed and cleaned periodically. Non-carbonate hardness is not removable by this method.

Another way to soften water is to pass it, cold, over zeolites,²⁰ described in the next chapter, where the subject of water softening is presented in more detail.

Mechanical Stokers. Hand shoveling of coal is still practiced, and smaller plants has much in its favor. In larger plants, mechanical stokers are used in order to save labor, but also to prevent smoke and to give a more uniform fire. The Taylor stoker has an inclined stationary grate; each "retort" has two rams or plungers, one above the other, and a number of retorts make up the stoker. Between the retorts a step-like surface is provided, with holes at each step through which the forced draft enters the fire. The upper ram moves fresh coal under the blanket of fire, so that the heat causes the volatile portions to pass out and over the bright fire where they are consumed, thus preventing smoke. The lower ram pushes the bulk of coal outward and downward toward the dumping platform. The motion of each ram is slight, only a few inches, and the strokes are 1 in 2 minutes (adjustable). The Taylor stoker belongs to the class of underfeed stokers.

There are a number of multiple retort underfeed stokers on the market, such as those manufactured by Westinghouse Electric Company and Combustion Engineering Company. An interesting and popular stoker is the spreader stoker, an overfeed type which distributes the coal from a point one or two feet above the grate at the front of the furnace by either mechanical or pneumatic means. Still another mechanical stoker is the chain grate, consisting of an endless belt as wide as the fireplace, moving very slowly toward the rear of the boiler. Fresh coal is fed by gravity to one end of the grate which carries it into the hot zone; at the turn, the ashes are dumped. The chain grate stoker operates either with natural draft or with forced draft.

A flue gas analysis indicates if proper burning takes place; no carbon monoxide should pass out as such, but should be burned to carbon dioxide. The excess of air should be small. Such analyses are made by means of the Orsat apparatus, carrying a measuring bulb and absorption pipettes. This control is used constantly, but is more important with hand firing than with mechanical stokers. The temperature of the stack gases is 500° to 600° F. (260° to 315° C.).²² If the load on the boilers is not steady, then, if steam is drawn off irregularly, it is important to alter the intensity of the fire by altering the draft; in case of hand firing, with natural draft,

²⁰ *Ind. Eng. Chem.*, 19, 445 (1927).

²¹ There are 3 absorption pipettes: a alkali solution for CO₂; b alkaline pyrogallol for oxygen; c ammoniacal cuprous chloride for CO.

²² For a complete heat balance sheet, see Marks, "Mechanical Engineers' Handbook," New York: McGraw-Hill Book Co., 1916, p. 898.

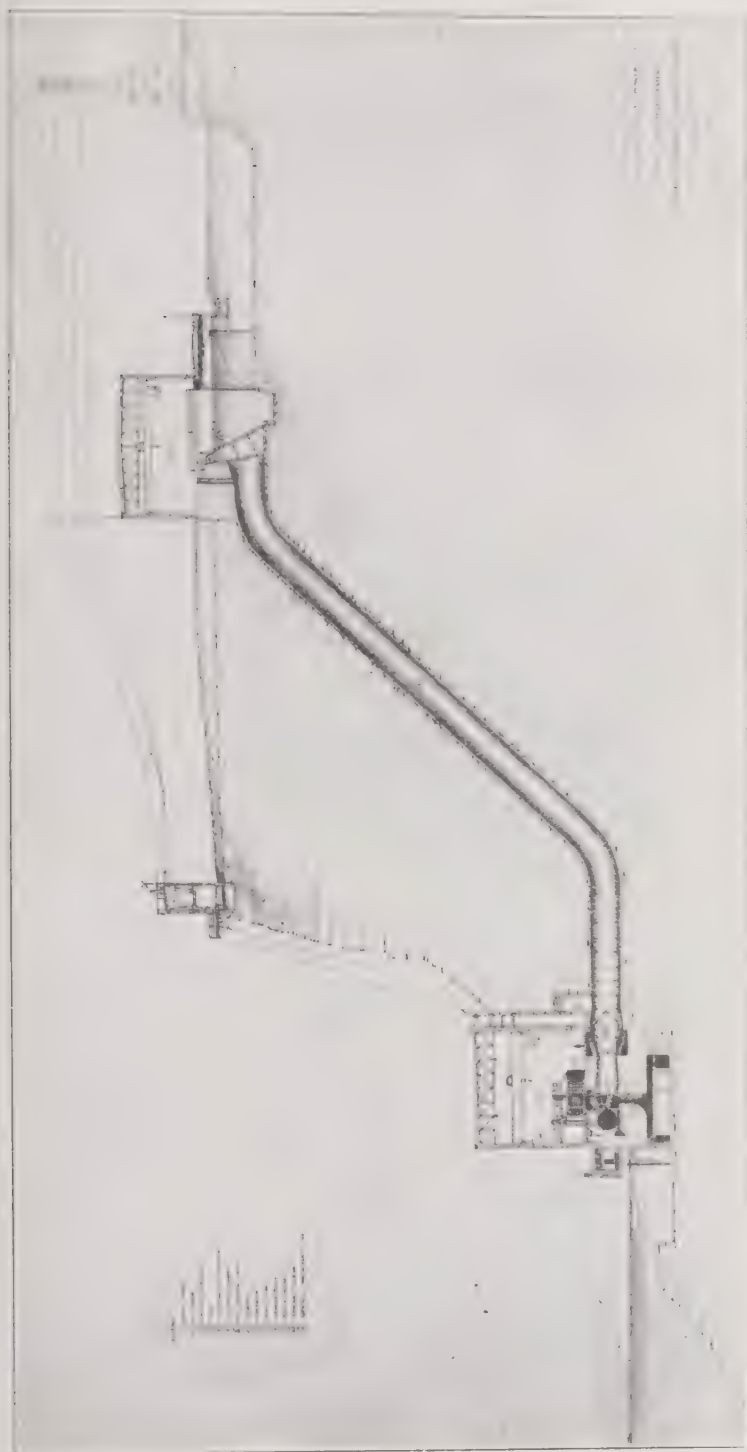


FIGURE 73.—The application of water to a turbine wheel; cross-section through the forebay and terminal basin of the hydraulic canal and tunnel, penstock cut in the rock, Johnson regulating valve, draft tube for escaping water, and generator. Niagara Falls Power Company Plant 3B, in the gorge. The difference in levels averages 217 feet. (By permission.)

Locke damper regulator is a simple equipment which responds quickly. Automatic carbon dioxide recorders are on the market.^{22a}

Even mechanical stokers are classed now with the developments of the past age; the most modern method of applying coal energy to the boiler is by means of powdered coal. A heavy-duty pulverizer is set close to the boiler, and is swept by a blast of air which carries the fine coal (through 200 mesh) into the burner, where it burns like gas or oil. A melted slag accumulates in the bottom of the boiler setting, and this is drawn off by tapping just as a blast furnace is tapped.

HYDROELECTRIC POWER

The utilization of water power to its full capacity is a modern development which had to wait until the science of generating electric current was sufficiently advanced. By means of the electric current, the enormous quantity of power developed in one spot, at a waterfall, for instance, may be distributed

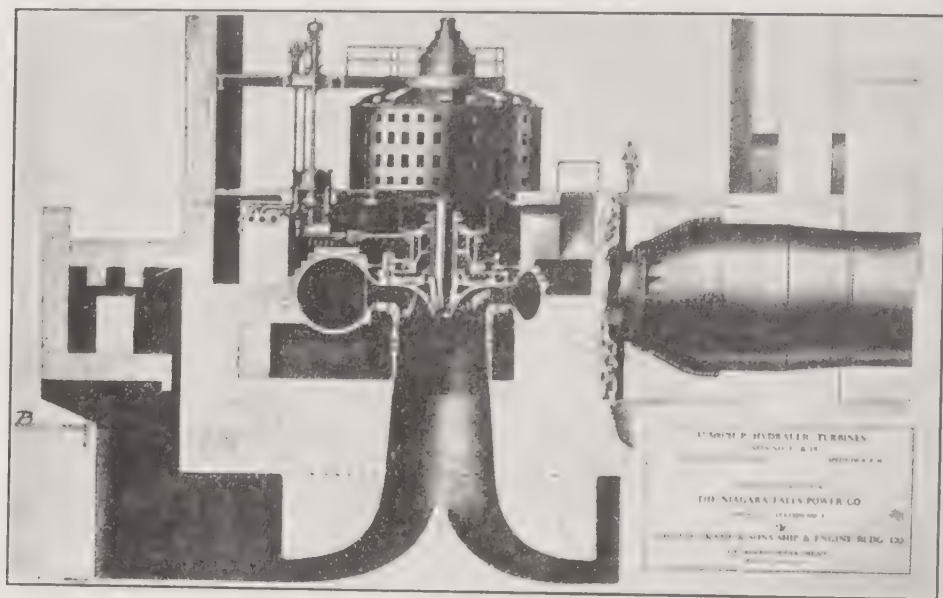


FIGURE 74.—Assembly of generator, water wheel and casing, and draft tube for the escaping water. The water from the penstock, at right, reaches the casing in the wider part first. Mean level of river shown at *R*. Niagara Falls Power Company Plant 3B. (By permission.)

tributed over a wide area many miles away. If water power had to be used as mechanical power (rope and belt drives), the present-day developments would not exist. Hydroelectric power is important because it is independent of a supply of coal. The cost of installation of a hydroelectric power plant may be greater than that of a steam power plant, but the running cost is lower. (See further.)

Water power is transformed into electrical power by applying the water to a wheel (turbine), which carries on the same shaft the pole pieces, for example, of an alternating-current generator; the armature is stationary

^{22a} For example the Ranarex, described in Chapter 46.

The opposite arrangement is used less often. At Niagara Falls, the voltage (12,000) for distance transmission, this current is raised to 60,000 volts in 11 transformers. Direct current is produced from the alternating current by applying it in the separate manufacturing plants to the motor of a direct-current generator. Water power may also be transformed directly to direct current.

The penstock brings the water from the upper level to the level at which the waterwheel is situated, and delivers it to a spiral casing surrounding the wheel. It enters the buckets of the wheel and escapes downward, best through a draft tube in which suction is developed which acts on the wheel by decreasing what might be called the back pressure. In the latest plant at Niagara Falls, the penstock is cut into the solid rock, lined with concrete (see Fig. 73). The second illustration (Fig. 74) indicates the relative location of penstock, casing, water wheel and generator; the third (Fig. 75)

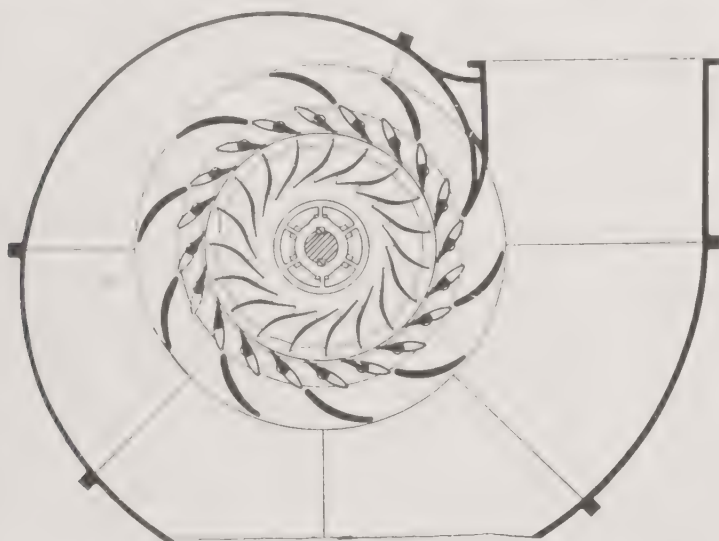


FIGURE 75.—Horizontal cross-section through water wheel, wicket gates, guide vanes, and casing. The water wheel is 16 feet in diameter, and its speed is 107 r.p.m. The water escapes downward. Niagara Falls Power Company Plant 3B. (By permission.)

gives details of the casing and water wheel. The generator shown develops 7,500 horse-power or 28,000 kilowatts (27,964). Hydrogenerators are built as large as 70,000 or more horsepower.

The capacities for the major hydroelectric power projects are shown in Table 24.

STEAM-GENERATED POWER

Steam is not usually generated from electric current, but a practical method for such generation has been described.²³ The opposite process, however, the generation of electric power from steam, is a universal one. A steam plant may be installed at lower first cost than a hydroelectric

²³ "The Electric Steam Generator," an article by Horace Drever, *Ind. Eng. Chem.*, 14, 923 (1922).

TABLE 24.—Capacities for the major hydroelectric power projects in kilowatts.
(Estimated, June, 1937, unless otherwise stated.)

	Present installed capacity	Ultimate installed firm power
Niagara river, at Niagara Falls	986,000 (Can.) 561,000 (N. Y.)	
Boulder Dam, Colorado river, 1912	869,800	1,000,000
Grande Coulee, Columbia river, 1912	344,000	2,520,000
Bonneville, Columbia river ^{22b}	86,400	688,000
Wilson Dam, Tennessee river	261,400	620,000
Norris Dam, Clinch river	132,000	235,000
Pickwick Landing Dam, Tennessee river	96,000	288,000
Wheeler Dam, Tennessee river	90,000	612,000
Chickamauga, Tennessee river	72,000†	210,000
Guntersville Dam, Tennessee river	68,000‡	134,000
Conowingo, Susquehanna river	378,000	594,000
Total potential capacity for the United States*..		80,000,000
Total installed capacity, U. S.*.....	20,000,000 ^{22b}	

The flow of the water over the year is steady for the Niagara River, fairly steady for the Colorado and Columbia Rivers; it fluctuates widely for the Tennessee and Susquehanna Rivers. In installed capacities, the states rank as follows* for 1936: California, 15.2 per cent of total; New York, 11.7; Washington, 6.4; North Carolina, 6.1; Alabama, 5.4; South Carolina, 5.; Maine, 3.8; New Hampshire, 3.6; Pennsylvania, 3.5; Georgia, 3.5.

* Geological Survey, January 6, 1936.

† To be completed in 1939.

‡ To be completed in 1938.

^{22b} The installed water power in the United States on January 1st, 1941, is given as 18,868,027 horsepower, equivalent to 14,072,500 kilowatts, by the Federal Power Commission. In 1938 there were 14,320 kilowatt generators in operation at Bonneville (quoted from 24c).

power plant, under ordinary conditions; it may be installed at any point to which coal may be hauled, and where there is an adequate supply of condensing water; it has the third advantage of being flexible, that is, its output may be reduced for any period of time, even for periods of an hour or less, with a corresponding reduction in coal. Hydroelectric power, on the other hand, cannot be shut down economically, for the raw material—the flowing water—passes at the same rate over the 24 hours. In the Buffalo District, the hydroelectric plants carry a base load; that is, load which is constant over the 24 hours of every day. A certain portion of the base load and all the peak loads are carried by a large steam plant of 622,000 h.p. By this combination, the most efficient use of both sources of power is made.

The modern method for generating electric power from steam is to produce the steam at high temperature and pressure from highly efficient pulverized-coal burning boilers and to apply this to a steam turbine with a horizontal shaft which is direct-connected to the field of an alternating current generator. For example, the newest generating unit of a large steam station²⁴ has a 17-stage turbine. Each stage consists of a turbine wheel with numerous stainless steel (Aseloy) buckets varying in length from 3 inches at stage 1 to 20 inches at the last stage, and also varying in width from $\frac{1}{2}$ inch to 2 inches or more. The buckets are set radially near the periphery, and a stationary piece, called the diaphragm, is mounted close to it; the diaphragm has similar curved buckets, set in the opposite sense which act as guides for the steam and send it into the curve of the rotating buckets just next to it. The speed is 1800 rpm, and the capacity of the generator is 80,000 kilowatts; the voltage is 12,000. Single-shaft generators

is built with capacities varying from 20,000 to 80,000 kilowatts. The steam is generated in one boiler, which produces 900,000 lbs. of steam per hour, at 1500 lbs. pressure, and at a temperature of 900° F. At the turbine inlet the pressure is about 1250 lbs., and the pressure drops in the successive stages until it leaves the last one at $\frac{1}{2}$ to 1 inch of mercury back pressure.



FIGURE 76.—Aerial view of Grande Coulee dam.

The unit just described is a condensing unit, which means that the last stage delivers to a surface condenser. The amount of condensing water necessary is considerable, amounting to approximately 60 gallons of water per hour for each kilowatt of capacity. There are also topping turbines which deliver at the last stage a stream of steam at an appreciable pressure, and work, for example, from a high of 1500 lbs. to a low of 250 lbs. without condenser. The 250-lb. steam may be used in various ways; in a power station it may be needed for application to suitable turbines, generally of older design, which themselves are condensing units.

The boiler and turbine combination here described will produce a kilowatt hour of electrical energy with 0.83 lb. of coal.

The average fuel equivalent for all the power generated by coal in 1940 was 1.37 lbs. of coal per kilowatt hour (Minerals Yearbook).

* Buffalo Niagara Electric Corp. Steam Plant, Huntley Station.

A few more words regarding the 900,000-lb. per hour boiler described may be of interest, and will complete the picture. (See Fig. 76a.) The boiler is better named a water-cooled furnace, or rather, a two-stage water-cooled furnace. The fuel is pulverized coal, crushed and ground close to the furnace, to minus 200 mesh, and swept into the primary furnace by a stream of preheated (moderately) primary air, the velocity of which is so adjusted that the flame forms about 1 to 2 inches away from the burner tip. The primary furnace is lined with studded tubes, covered with a plastic refractory, chromore. In the secondary furnace, part of the tubes at least must be of the block type; these are the longest tubes. The water is distilled but nevertheless there is a softening treatment, and also an oxygen-destroying treatment with sodium sulfite. The blowdown is continuous. The furnace has a superheater, which in this construction is of the draining type, an economizer, and an air heater in the flue gas which furnishes 500° secondary air. The ash in the form of slag is tapped periodically, as already suggested in a previous paragraph, but here the hot slag strikes a water table (made up of high-velocity jets of water) and is disintegrated, so that it can be pumped away in granulated form. A 66" drum at the top of the boiler acts as a storage reservoir for the water in the boiler. If the steam output of this large boiler were to decrease suddenly, the pressure would suddenly increase. The increase in pressure would decrease the volume of the steam bubbles which are constantly being produced in the water walls of the boiler. The reservoir action of the drum instantly supplies water to the boiler tubes to take up the space made as a result of the collapsing steam bubbles. If this water was not supplied instantly, serious damage might result from overheated tubes. Another purpose of the drum is to provide a means of separating the steam from the water. For most efficient operation, the steam leaving the drum should contain as little water as possible. The drum contains "scrubbers" and "cyclone separators," enabling it to deliver dry and clean steam to the superheater. Two large pipes (3 inches) carry water from the upper drum to the lower headers feeding the long vertical tubes; the circulation of the water is down these two pipes and up the long tubes to the upper drums. The over-all height of the boiler is that of a five-story building. An elaborate instrument board gives a vital information instantly.

Mercury vapor has been used as the working substance in a boiler and turbine for several years, and on the experience gained thereby, three new improved *mercury vapor systems* have been installed at Hartford, Conn. Kearny, N. J., and an outdoor station at Schenectady.

In the original 1928 installation, an over-all thermal efficiency of 33 per cent was obtained through the year. In the new ones, it is expected that 36 per cent will be reached. In a porcupine boiler, with cylindrical finger-like extensions on its lower part, and preheated, mercury is vaporized by direct heat from an oil burner or pulverized coal burner; a temperature of 885° C. (1625° F.), under a pressure equivalent to a column of liquid mercury 17 feet high, is recorded. The mercury vapor drives a turbine; the exhaust vapors pass to a steam boiler, in which 400 lbs. of steam is raised. The steam is superheated and drives a turbine also.

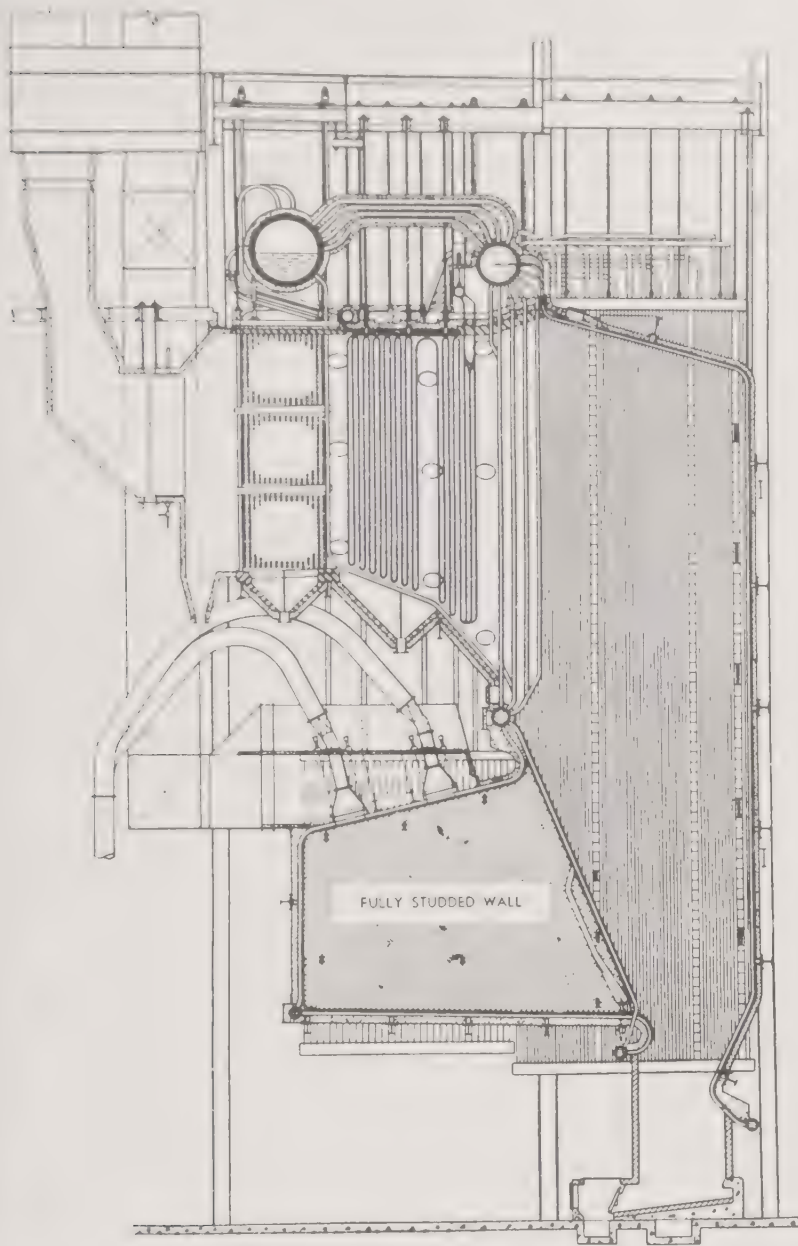


FIGURE 76a. A two-stage water-cooled furnace, of the slag-tap type. The primary furnace has stud-tubes for its walls; the secondary has block tubes. The conventional boiler heating surface is largely eliminated. The fuel is pulverized coal, applied as shown. This unit develops 605,000 pounds of steam per hour at 1475 pounds pressure and 950° F. total temperature. Note the superheater, below and between the drums; the three sections of the economizer to the left of superheater, and the air heating unit to the left and above the main drum. (Bulletin G-16, p. 24, "Water-cooled Furnaces," The Babcock and Wilcox Company, 1515 Guardian Building, Cleveland, Ohio.)

The cost of *steam-generated electrical power* depends upon a number of factors, one of which is the cost of coal. Coal at the mine has been, at least until just recently, about \$2.00 per long ton (\$1.854 in 1939, Minerals Yearbook). To this must be added the cost of freight which, to many localities, equals and even surpasses the mine cost. In 1940 and again in 1941 there was a relatively sharp advance in the price of coal.

For this reason, steam plants situated at the mines, and called *mine-mouth plants*, have a great advantage, especially if the power is used at the spot or close by; for if the current must be transported, a cost of transmission appears which takes away some of the merit of such a station. The cost of transmission over a distance of 200 miles is computed as 2.2 mills per kilowatt-hour; over 100 miles it is 1.92 and over 50 miles 1.0. Mine-mouth plants are comparatively rare, partly because a second requirement is an abundance of cooling water, and this is not often fulfilled; rather it is more common to find that steam power plants are almost always located where there are large and cheap supplies of condensing water, for it is much cheaper to haul coal to the plant than to transport water.

Prices for electrical power vary in different localities; for industrial use firm power on contract at \$18 a horsepower year was considered fair a few years ago. Firm power means a stated number of kilowatts at all times; there is no opportunity to vary as a householder does who buys on the meter. \$18 per horsepower year is equivalent to 2.75 mills per kilowatt hour. It is said that the Rjukan development in Norway, part of the Norwegian Hydro, using water from a natural lake at the head of a river which drops 2000 feet in a short distance and sending the water through two powerhousees a few miles apart, develops power for \$3.00 per horsepower year.^{24b} This is probably the most favorable figure in the world. By moving into isolated places with favorable conditions of head and volume of water, and with no requirement of dam building, a cost of \$10 to \$15 per horsepower year may be achieved. The large government plants will and do already furnish firm power for similarly low figures. Power at Bonneville, for which rates have been approved by the Federal Power Commission, will be obtainable as firm power for \$14.50 per kilowatt year, equivalent to \$10.81 for the horsepower year. The rates at Boulder Dam, up to May 31, 1942, were 1.163 mills per kilowatt hour for firm power, equivalent to \$10.19 per kilowatt year, measured at the power plant; secondary energy 0.34 mill per kilowatt hour.

The *cost of steam-generated power* depends upon the cost of coal, as already mentioned, upon the fuel efficiency, for which figures have been given, upon the installation cost per unit of power, upon the load factor and other factors. As to the investment cost, it was estimated in 1937 that the initial investment for a steam plant is \$83 per kilowatt hour to be produced, and for a hydroelectric plant \$250 per kilowatt. As to the latter figure, the estimate of \$126 per kilowatt is made in a study by the Power Authority of the State of New York; as to the former figure, the Authority computes that \$93 per kilowatt of installed capacity is as low a figure as can be taken (1937).

^{24b} *Ind. Eng. Chem.*, 28, 146 (1936).

In comparing hydroelectric power with steam power, it is unwise to generalize, because installations are unlike each other, and differ especially in favorable and unfavorable factors.^{24c}

COLD PRODUCTION OR REFRIGERATION

Temperatures just above the ice point, and below, are reached chiefly with the aid of chemical refrigerants. Arranged in the order of their importance, the substances used are anhydrous ammonia, carbon dioxide, sulfur dioxide, methyl chloride, ethyl chloride, and paraffin hydrocarbons. Ammonia is by far the most commonly employed refrigerating agent; it is used for ice manufacture, for cold storage of meats, fruits, vegetables and dairy products, and for general refrigeration.²⁵ Carbon dioxide is a somewhat less efficient agent; it is used instead of ammonia when the odor of the latter in case of leak would be objectionable, for instance in hotels, in some hospitals, and on board ship. It is used also for temperatures below those which ammonia can furnish. Sulfur dioxide is the most generally used "working substance" for household refrigerators; for the same purpose, but less generally, methyl chloride is utilized. Paraffin hydrocarbons, *i.e.*, ethane, propane, butane, and isobutane, are used only in special cases. With any of the agents listed, the method consists of compressing the gas sufficiently so that on cooling with ordinary cooling water, it will liquefy, and then sending the liquid, still under pressure, to an expansion valve leading to coils in which the expansion takes place; heat is abstracted from the surrounding liquid or room, to make the expansion of the liquid to gas possible. The expanded gas is compressed, and sent through the system again. The same material serves over and over; only the losses due to leaks must be replaced.

The boiling points at atmospheric pressure for the various working substances follow:²⁶

Ethyl chloride C_2H_5Cl	+ 55° F. or +12.5° C.
Sulfur dioxide SO_2	+ 14 or -10
Methyl chloride CH_3Cl	- 11 or -23.9
Dichloro-difluoromethane, CCl_2F_2	- 21.6 or -29.8
Anhydrous ammonia NH_3	- 28 or -33.3
Propane C_3H_8	- 49 or -45
Carbon dioxide CO_2	-108.8 or -78.2

For an ammonia system, cast-iron, wrought iron, and steel are used; copper and brass are avoided. The essential parts for a refrigerating plant using brine as an intermediate cooling substance are shown in Figure 77.

^{24c} "Government Hydro Versus Private Steam Power," a study in relative economy, prepared by the Power Authority of the State of New York and submitted to the President on November 22, 1937. This study provides the only published report on the relative economy of hydroelectric power and steam power; it embodies figures submitted by a private consulting engineer, Mr. F. F. Fowle, Dean of Engineering at Purdue University, and also criticisms and corrections by the members of the technical staff of the Power Authority of the State of New York. The original figures of Mr. Fowle showed 6.3 mills per kilowatt hour as the cost for steam power, and 6.3 mills for hydroelectric power. The Authority representatives alter the figures after a number of considerations, so that the steam power figure reads 6.3 mills, while the hydroelectric power reads 2.1 mills. According to Mr. Fowle, steam power is cheaper, 4 mills versus 6 mills; while according to the Authority representatives, hydroelectric power is cheaper by much more, 2.1 mills against 6.3 mills. The reader is referred to the study for additional data.

²⁵ This is separated from oil by ammonia refrigeration (Chapter 24); for the liquefaction of chlorine the ammonia or carbon dioxide may be used (Chapter 5).

²⁶ For explosion limits and physical properties other than boiling point consult "Properties of Gases," Circular 2, 1926, American Society of Refrigerating Engineers, 37 West Thirty-ninth Street, New York.

The pressures are moderate; on the high-pressure side, the gas is compressed to 155 lbs., with a temperature of 210°F. (99°C.). The gas is cooled to 75°F. (24°C.), with the pressure maintained near 155; it liquefies and collects in a receiver. A small stream is sent through the expansion valve (an ordinary iron globe valve) to the low-pressure coils, where the liquid turns to gas, absorbing heat from the brine. The brine is circulated through a suitable system of pipes (pump). A temperature of 15°F. (-9.4°C.) for the brine is usually reached. The gas returns to the compressor with a pressure of about 20 lbs.

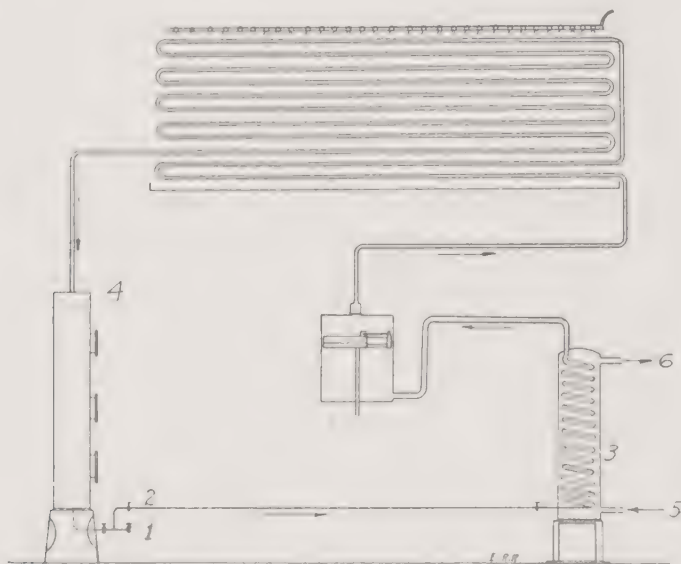


FIGURE 77.—Refrigerating plant with ammonia as working substance. Fresh supplies from purchased cylinders are introduced at 1 into the receiver 4; the liquid enters the cooler, vaporizes, and reaches the compressor and from there the condenser. The liquefied ammonia collects in receiver 4 and is used over again. The brine enters the cooler 3 at 5, and leaves at 6; brine circulation not shown.

The sources of ammonia are discussed in Chapters 6 and 14.

In the liquid carbon dioxide refrigerating system, the pressure on the high-pressure side (condenser) is 1000 lbs.; on the low-pressure side (expansion coils) 300 lbs. per square inch. The condenser temperature must be as much below 88°F. (31.1°C.), the critical temperature,²⁷ as possible.

CARBON DIOXIDE

Sources

Carbon dioxide is used commercially as a gas (soda ash manufacture), compressed as a liquid in steel cylinders (soda fountains, for refrigeration and as convenient source of the gas), and as the solid. It is obtained from (1) the combustion of coke; (2) the calcination of limestone; (3) as a by-product in syntheses involving carbon monoxide; (4) as a by-product

²⁷ The critical temperature is the temperature above which the gas cannot be liquefied, no matter how great the pressure; see also footnote 31.

fermentations, (5) by the action of sulfuric acid on dolomite, (6) from cokes.²⁸ Gas from any one of these sources may be made into the gaseous, liquid, or solid form of carbon dioxide.

The utilization of the carbon dioxide in the combustion gases of coke involves the alternate formation and decomposition of alkali bicarbonates in solution. Hard coke is burned under boilers, and the fuel gases are so regulated that a maximum content of carbon dioxide, 16 to 17 per cent, is obtained. The gases enter a scrubber (tower) packed with limestone to remove sulfur compounds and fed with water to cool the gas and arrest the dust. The cold gases enter the absorber, a tower packed with coke down which a solution of potassium carbonate passes; carbon dioxide is absorbed, and the saturated solution is run to a boiler where the absorbed gas is liberated by heat. It is under this boiler that the coke is burned. The operation is continuous; charged solution flows in constantly, while the spent liquor is run off constantly. By means of an interchanger, the outgoing liquor heats the incoming liquor to some extent. The outgoing liquor, cold, returns to the absorber. The gas from the boiler is very pure. It is dried in a calcium chloride tower, and compressed to 100 atmospheres, at which pressure it liquefies at ordinary temperatures. (See Fig. 78.)

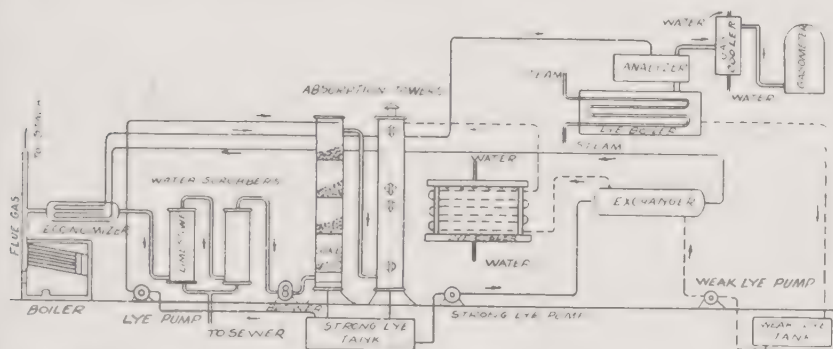


FIGURE 78.—Diagrammatic flow-sheet for the absorption of carbon dioxide in the fire gases from burning coke. The gas dissolves in a strong lye solution, from which it is driven out by heat, giving 100% CO_2 gas. (Courtesy of the Frick Company, Waynesboro, Pa.)

The other sources are presented in their proper places, except source (5), which is unusual. In Georgia,²⁹ a deposit of dolomite is mined, and the crushed rock treated with sulfuric acid in carbonators provided with a cover and gas outlet. The residue in the carbonators is a solution of magnesium sulfate, in which calcium sulfate is suspended. By keeping the solution on the acid side, no detectable quantity of calcium salt dissolves. The solution is made into Epsom salts, $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$, a laxative, and a material which serves in the leather industry. The carbon dioxide is compressed to the liquid and used in the preparation of carbonated beverages.

In addition to the uses which have been mentioned, carbon dioxide serves

²⁸ "Solid carbon dioxide from Mexico." James Welford Martin, *Ind. Eng. Chem.*, 23, 256 (1931).

²⁹ "Manufacture of carbon dioxide and Epsom salts." W. P. Heath, *Ind. Eng. Chem.*, 22, 437 (1930).

as a chemical in the manufacture of salicylic acid, white lead, and other products, as well as in fire fighting devices of various kinds. Fire extinguishers of the wall type, also called the soda-acid type, contain $2\frac{1}{2}$ gallons of saturated sodium bicarbonate solution and 4 ounces of concentrated sulfuric acid in a small bottle. On inversion, the acid reaches the solution and liberates carbon dioxide; the pressure developed expels the liquid through a nozzle to a distance of 30 to 40 feet. The main extinguishing agent is the water. Liquid carbon dioxide under pressure in steel cylinders may be released so that a carbon dioxide snow forms which may be directed into the gaseous blanket over the fire. The "firefoam" extinguisher system relies upon the smothering action of a foam blanket produced by the interaction of a sodium bicarbonate solution with an alum solution, in the presence of a foam stabilizer.

Solid Carbon Dioxide

One of the new refrigerants obtainable in commercial quantities is solid carbon dioxide. It is supplied in block form resembling the familiar artificial ice cake. Its uses are similar to the uses of ice, but it functions without melting, and without producing drips; it vaporizes, and leaves only gas, which may be easily vented, so that it has received the rather apt name of Dry Ice. Its manufacture will be described for the case of a plant particularly well situated with regard to its source of raw material.³⁰

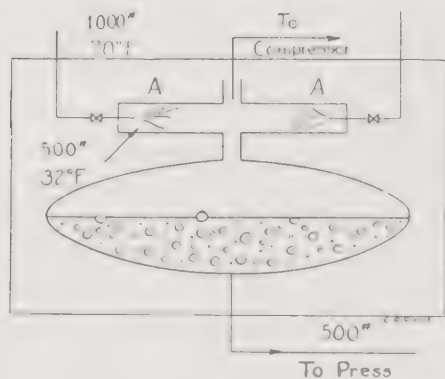


FIGURE 79.—The "evaporator," in which the liquid carbon dioxide is formed and stored.

Pure, liquid carbon dioxide under a pressure of 1000 pounds and at a temperature of 70°F . (21°C .), is delivered to the plant by a pipe system. It is sent to the "evaporator" (Fig. 79), where its pressure is reduced to 500 pounds, with a simultaneous drop in temperature to 32°F . (0°C). With the pressure set at 500 pounds, the liquid maintains itself at that temperature; as this is lower by several degrees than the room temperature, heat flows in and causes the liquid to simmer quietly. About 25% of it boils away. The vaporized portion is sent to a special compressor which delivers it as gas to the main compressor gas line, at a pressure of 1000 lbs.

The 32°F . liquid from the evaporator is admitted to the press chamber (Fig. 80); these have movable tops and bottoms, worked by hydraulic pressure. The chamber is 20 by 20 inches, and 24 to 30 inches deep. The liquid enters through an ordinary nozzle; part of it expands to gas, and

³⁰ The Dry Ice Corporation's plant at Niagara Falls, N. Y.

draws its heat largely from the incoming liquid, which is thus solidified to a fluffy snow. The gas formed is drawn off constantly by the suction of the main compressors and recompressed. By operating the top and bottom walls, the snow is compacted to a solid block 20 by 20 by 10 inches. Each press makes 6 to 8 cakes per hour. The density of the resulting cake is controlled by the amount of snow pressed into the 10-inch space. After discharge to a conveyor, the block reaches band saws, which cut it into six smaller blocks, each a 10-inch cube, weighing about 20 pounds. This is wrapped in brown paper and stacked in a specially insulated railway car for transportation to distant points, or into trucks for local delivery.

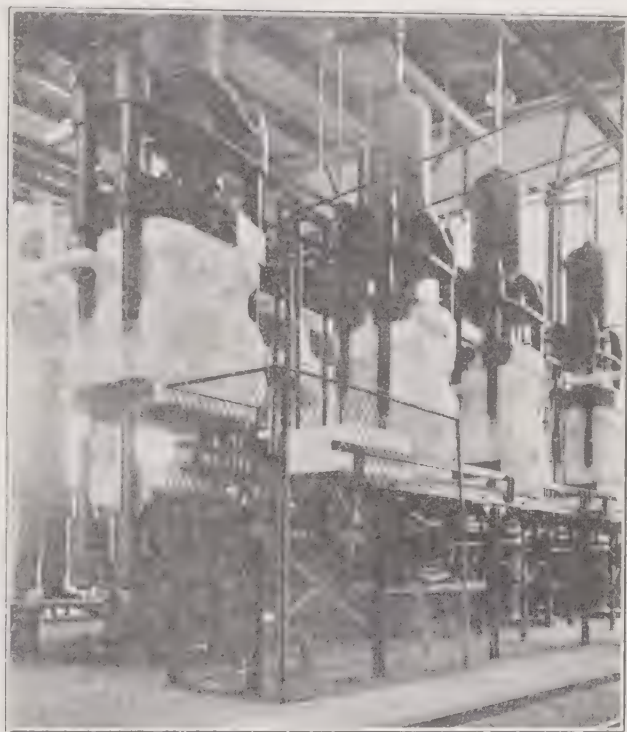


FIGURE 80.—Press chambers, in which the carbon dioxide snow is pressed into blocks; one of the blocks may be seen on the conveyor. (Courtesy of the Dry Ice Corporation of America, New York.)

Of the liquid delivered to the press, 20 to 45 per cent is solidified; the rest turns to gas and must be reliquefied. The colder the temperature of the liquid CO_2 and the colder the press chest, the higher the percentage frozen. Based on heat content, it is found that it takes 3.75 pounds of liquid to produce 1 pound of solid. The expansion in the chest is due to atmospheric pressure.

The critical temperature³¹ of carbon dioxide is 88° F. (31.1° C.), the critical pressure 1073 pounds. At 70° F. (21° C.), it is considerably below the critical temperature, so that a pressure of 1000 to 1100 pounds suffices to keep it in the liquid state.

³¹ The critical temperature is the temperature just above which no pressure, no matter how great, will liquefy the gas; the critical pressure is the pressure which just suffices to liquefy the gas at the critical temperature.

It will be clear that much of the expense in the plant will be that of recirculating the carbon dioxide gasified at the presses. The compressors are four-stage machines: 0 to 5 lbs., 65 to 70 lbs., 300 to 325 lbs., and 1000 to 1100 lbs. From the last stage the gas enters oil-removing filter, then a condenser cooled with tap water, which reduces its temperature to about 70° F. (21° C.). In the condenser, the carbon dioxide liquefies, and enters the "evaporator" with the new liquid, at the same temperature and pressure.

Carbon dioxide from any sources may be made into the solid form.

The uses of solid carbon dioxide are, at present, mainly for the preservation of foods. A railway car may be loaded with its perishable fruit, meat or vegetables, and a given number of blocks of Dry Ice placed on top of the goods so that the vapor will pass downward and form a heat-consuming blanket. The temperature attained is lower than with ice and salt mixtures, and may be regulated by the amount of Dry Ice per car. The shunting of the train to sidings for re-icing while en route becomes unnecessary: a single loading at the point of shipment suffices (for the average trip). Eighty-five per cent of the consumption is for ice cream cooling. The effective refrigeration from 1 pound of solid carbon dioxide when subliming at 0° F. (– 18° C.) is 244 B.t.u. A temperature as low as – 108.8° F. (– 87.9° C.) may be reached by allowing the solid carbon dioxide to evaporate at atmospheric pressure. A lower temperature still is obtained when evaporating at reduced pressure; hence a means is provided of reaching and maintaining low temperatures without any machinery.

In order to expand, the industry needs no machinery nor complicated processes of manufacture, but new uses, either as a refrigerant, or as a source of gas.

QUICK FREEZING OF FOODS

Refrigeration has been employed in the meat industry, in cold storage houses for the preservation of butter, eggs, vegetables, fruit, and other perishable foods. A new kind of refrigeration is now applied to sea food, particularly fish fillets, and to fresh vegetables and small fruit; they are not only cooled, but frozen. The fillets of fish, for example, are laid in the packing paper, are held between two flexible non-corroding metallic belts and pass between sprays of brine at – 45° F. (– 42° C.); they leave the belt frozen, to be stored or shipped at once. If to be shipped, the fillets may be packed in corrugated fiberboard boxes which insulate sufficiently to keep the fish frozen for 4 to 5 days, and fresh for several days longer. The frozen foods may be stored at temperatures low enough to keep them in the frozen state.

There is an increasing demand for house refrigeration, to keep its temperature at a comfortable point. This subject is related to humidity relations, and is therefore discussed in Chapter 46.

Iceless Refrigerators. The various kinds of electric refrigerators which are displacing ice chests are operated on the same principle as the ammonia refrigerating machine, but on a small scale. The working substance may be sulfur dioxide, methyl chloride, ammonia, a hydrocarbon, dichloro-difluoride.

methane, or other suitable agent; it is compressed by small motor-driven compressors. The heat of compression is removed by a current of air or by a trickle of water. The liquid so formed is then expanded, consuming heat which is drawn from the chest and its contents. The gas is then recompressed, and put through the next cycle.

Silica Gel Refrigerators. Other types absorb a vapor in silica gel,³² or other solid absorbent, and use the heat of evaporation of the liquid for cooling. After the gel is saturated, its adsorbed mass is driven out by heat, thus revivifying the gel; in the meantime, a twin unit carries the load.

OTHER PATENTS

U. S. Patents 2,040,407 and 2,040,406, chemical heating composition, to produce heat by chemical action.

PROBLEMS

1. A swimming pool with an area of 25 feet by 70 feet contains water to an average depth of 7.13 feet. Find the cubical content and the weight of the water it contains. The water enters at a temperature of 45° F., and must be heated to 68° F. How many pounds of coal are needed to furnish that heat, if 73 per cent of the heat value in the coal reaches the water in the pool? How many gallons of fuel oil, if its specific gravity is 0.9, and the efficiency of heat transfer the same as for coal? For the same pool, at another season, the water enters at 32° F., and must be heated to 68° F. How many pounds of anthracite must be burned and used, if 73 per cent of the heat value in it reaches the water? All necessary heat values and conversion figures will be found either in this chapter or in the appendix.

2. Dry ice in Los Angeles can be made purer and just as cheaply from CO₂ from combustion of natural gas as from the gas wells developed in several places. This is due to the fact that the power which can be generated by burning natural gas under boiler is just about sufficient to compress the CO₂ which can be recovered from the dry gas.

A dry ice plant burns natural gas (CH₄), absorbs the CO₂ formed in Na₂CO₃ solution, and recovers and compresses the pure CO₂, forming a 220-lb. cake of dry ice every 10 minutes.

(1) Assuming only 50 per cent of the CO₂ formed to be recovered, what volume (cu. ft.) of CH₄ is burned per hour? (60° F., atm. press.)

(2) Assuming weights of 90 lb./cu. ft. for dry ice and 57 lb./cu. ft. for water ice, and refrigerating effects of 275 B.t.u. and 155 B.t.u. respectively, what weight of dry ice is equivalent to a ton of water ice, and what volume (cu. ft.) will each occupy?

(3) If dry ice costs \$0.02/lb., what is the equivalent value of the water ice?

(4) If the soda liquor starts at 9.0 lb. Na₂CO₃/cu. ft. and 60 per cent is carbonated to NaHCO₃ and 20 per cent remains as NaHCO₃ at the discharge from the evaporator, how many cu. ft. of liquor (neglecting volume changes) must be carbonated per minute to handle the above production?

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The inhabitants of a city must have a plentiful supply of water for drinking, cooking, washing, and sanitary purposes. It is one of the few public services to which the American can point with pride. The largest city in the country brings its water 92 miles—water which is palatable and safe all periods of the year. A second problem which the congregation of so many people in cities has raised is that of sewage disposal; in its solution, it is gratifying to contemplate that an American chemist, Dr. H. W. Clark, of the Massachusetts Board of Health, has played a major rôle by his discovery of the principles of the activated sludge process.

Chapter 13¹

Water for Municipalities and for Industrial Purposes. Sewage Disposal Plants

In every city, a supply of water is provided for domestic, public, and industrial uses. The chemical industries at times require water which meets certain specific requirements; in some cases it must be free from even traces of heavy metals; in others, its purity is of no moment, but it must be cold year round. The industries situated within reach of the city water draw their supply, or at least part of it, from the city main. For that reason, water for municipal purposes will be considered first, and subsequently the additional demands made by the industries.

WATER FOR MUNICIPAL PURPOSES

A water for municipal purposes, for drinking, for general domestic and industrial consumption must be (1) hygienically safe, (2) reasonably soft, (3) practically colorless, and (4) free from objectionable odor and taste.

Absolutely pure water, consisting only of H_2O free from any dissolved matter, and optically void, is a laboratory curiosity, and most difficult to prepare; such a water would be soft, colorless, odorless, and would have a hardness value of 7. It is the latter requirement which is difficult to meet, for the presence of carbon dioxide lowers the pH . Rain water collected in a cistern would be soft; it is still the custom in the country to build such cisterns in order to have water which soaps easily for the washing. In Bermuda, all drinking water and water for washing is rain water, collected on the roofs of the dwellings. River and lake waters are surface waters; they are comparatively soft (that is, low in mineral content), and are most likely to contain easily soluble salts and sediments. Ground waters, from artesian wells, for example, are usually free from suspended matter, but are much harder (that is, richer in calcium and magnesium salts) than surface waters in the same vicinity. In regions of heavy rainfall, the surface waters contain less mineral matter, because of dilution. Sea water is not water at all, in comparison to the waters just discussed, but a salt solution. It contains 3.5 per cent salts, of which 80 per cent is common salt, NaCl . This is an enormous concentration, yet it must be added that, nevertheless, sea water

¹As to water, in collaboration with Dr. Benjamin F. Clark, of Niagara Falls, N. Y.

is used industrially; for example, in turbine steam surface condensers plants located at the sea shore. In surface waters and ground waters, amount of impurities is so small that it is expressed not in per cent, but parts per million (ppm.), as for example, 300 ppm., which means 300 grains dissolved matter in 1 million grams of water. Roughly speaking, sea water is 100 times more concentrated.

In considering soft waters and hard waters, it is well to classify them closely, and in figures:

Soft water contains less than 100 ppm. total solids.

Medium hard water contains from 100 to 200 ppm. total solids.

Hard waters contain from 200 to 500 ppm. total solids.

Saline water contains 500 ppm. and over total solids.

"Parts per million total solids" means the residue on evaporating water on a steam bath. The classification just given is a quantitative one, but to most chemists, hardness does not mean merely a comparatively large amount of total solids, but the presence of salts of calcium and magnesium which, with a soap solution, do not allow foam formation until they are precipitated as insoluble soaps. In general it so happens that the residue solids for medium and hard waters are over half calcium and magnesium compounds, so that the figures reflect the amount of these salts as well as the total for all salts. With saline waters, it is different; here the total solids are likely to be mainly sodium chloride.

The methods practiced for the purification of water for municipal purposes will be shown by means of several examples.

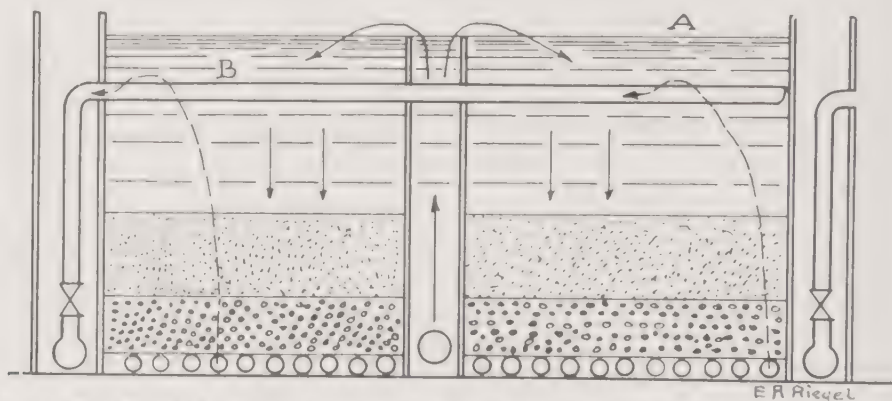


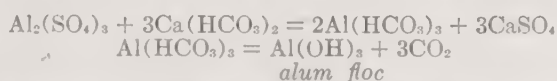
FIGURE 81.—Sand filter, to show method of washing. The water to be filtered enters as shown by full arrows, and passes through sand, gravel, and underdrains to clear wells (not shown); this water reaches level A. To wash, the flow is reversed; water enters through the underdrains, rises through gravel and sand, and leaves through gutter B. At such times, the level of the water stands at B. (Buffalo Filtration Plant.)

Buffalo Municipal Water Filtration Plant. For Buffalo, water is drawn from Lake Erie, at a point at the head of the Niagara River. The water enters a tunnel one mile long, 12 feet by 11½ feet in cross-section, through 12 ports, each 6 feet square, opening 20 feet below the surface of the lake. The tunnel runs into a canal which feeds the "low lift" centrifugal motor.

ten pumps which deliver the raw water to the coagulating basin against a head of 17 feet, through the raw water discharge conduit. In this conduit, in Venturi tubes, 70 inches by 48 inches, meter the water. "Filter alum" added at this point, at the rate of 50 pounds to 1 million gallons. The water is distinctly alkaline, so that aluminum hydroxide, the alum floc, forms without other addition. The water moves slowly through the coagulating basin, taking a zigzag course set by baffle plates. The basin is 300 feet long, 100 feet wide, and 25 feet deep. After 3 hours, the water leaves it and passes to the sand filters.

There are 40 filters, each 53 feet by 33 feet in area. Perforated underdrain pipes are covered by 16 inches of gravel made up of five graded layers, and overlaid by 26 inches of sand (grain size 0.38 to 0.45 mm.). The filter capacity is 2 gallons per square foot per minute, 4 million gallons per day for one filter, and 160 million gallons per day for the plant. The filter capacity is the capacity for the station; the low-lift pumps have a 50 per cent excess capacity, the tunnel a 180 per cent excess capacity. The filtered water passes to clear wells, and flows through a canal to the pumping station. The chlorine is injected in the canal, at the rate of 2 pounds per million gallons.

The reaction between the "filter alum" $\text{Al}_2(\text{SO}_4)_3 \cdot 18\text{H}_2\text{O}$ and the alkalinity in the water, in the form of calcium bicarbonate, is:



The alum floc is voluminous; as it slowly settles, it carries with it most of the suspended matter, and a part of the bacteria (the count is reduced about half). The choice of the coagulant is a particularly happy one in other respect. A part of it is in the colloidal state, with a positive charge in the colloidal sense, so that it is most efficient in precipitating the naturally occurring colloidal materials in the water, which are almost exclusively negative.²

In the clear water conduit a Venturi meter 12 feet by 6 feet records the volume of flow. The station is amply provided with level gages, meters, and pressure recorders; every filter has a set of instruments.

About 15 per cent of the suspended matter, including the alum floc, settles out in the coagulating basin; the rest is caught by the filter. After 24 hours, the filters are rid of their dirt by reversing the flow of the water, so that it rises through the sand and empties into gutters which, while the filter is working normally, are submerged. This muddy water is delivered downstream from the intake. The washing requires 10 minutes. The coagulating basin is divided into two independent halves, so that it can be cleaned without interruption of the service; this is done twice a year. One and one-half per cent of the filtered water is consumed in washing the filter beds.

² The precipitation of a negatively charged colloidal suspension by a positively charged colloidal reagent is called *mutual precipitation*. The positive colloidal particle is $[\text{Al}(\text{OH})_3]_n^{+}$. For a full study, see the chapter "Chemistry of Coagulation," in "Chemistry of water and sewage treatment," by A. M. Buswell, New York, Chemical Catalog Co., Inc., 1928.

Municipal Plant at Birmingham (Alabama). At the Birmingham tion, an unusual impurity is removed and made to share in the water purification; this impurity is manganese. During the late autumn, when the level of the supply reservoir (Lake Purdy) has been lowered considerably, the content of manganese in the water rises abruptly. The raw water before being treated with a coagulant, which is aluminum sulfate in this case, is treated with sufficient chlorine to convert all the manganese present into the chloride; this is hydrolyzed by the alkalinity of the water, and forms a flocculent precipitate. This precipitate assists in the clarification action of the aluminum hydroxide, and in this way this undesirable impurity is removed, and at the same time functions as coagulant, allowing a corresponding amount of aluminum sulfate to be saved.

TABLE 25.—*Analyses of Birmingham, Ala., Water.*

	May, 1932	October, 1931
Total solids	140 ppm.	124 ppm.
Total hardness, as CaCO_3	67	107
Iron (Fe)	0.07	0.01
Calcium (Ca)	17	33
Magnesium (Mg)	5.9	6
Sodium (Na)	19	4.1
Potassium (K)	1.3	1.2
Carbonate (CO_3)	0	0
Bicarbonate (HCO_3)	54	120
Sulfate (SO_4)	61	15
Chloride (Cl)	2.0	2.0
Nitrate (NO_3)	0.45	0.40
Silica (SiO_2)	7.80	5.80

During the greater part of the year, the "filter alum" added is 0.7 to 0.8 grain per gallon of water; a small amount of lime is introduced when necessary, to keep the pH value near 6.9. Table 25 gives typical analyses.

Other Plants. At Marseilles, France, an apparatus for the sterilization of the city water by means of ultraviolet rays (instead of chlorine) has been in operation for some years and has proved highly satisfactory. The primary requisite for such treatment is a source of cheap electric power.

TABLE 26.—*Average analysis of the water furnished the Metropolitan Water District of Southern California beginning June, 1941, to date (May 1, 1942), from a lime-zeolite softening and filtration plant, fed with Colorado River water. The District includes Los Angeles.**

Calcium (Ca)	19
Magnesium (Mg)	9
Sodium (Na) and (K)	219
Carbonate (CO_3)	20
Chloride (Cl)	96
Sulfate (SO_4)	380
Boron (B)	0.1
Fluorine (F)	0.3
Silica (SiO_2)	9
Total dissolved solids	753
Total hardness, as CaCO_3	85
Carbonate hardness, as CaCO_3	33
Non-carbonate hardness, as CaCO_3	52

* Kindly supplied by Mr. Julian Hind, General Manager and Chief Engineer, The Metropolitan Water District of Southern California.

New Orleans (Louisiana) takes its water from the Mississippi; the food for coagulation is 24 hours (compared to the usual period of 2 to 6 hrs) because of the very fine sediment in the water. In Table 26, information on the Colorado river water, as it is delivered to Los Angeles is presented.

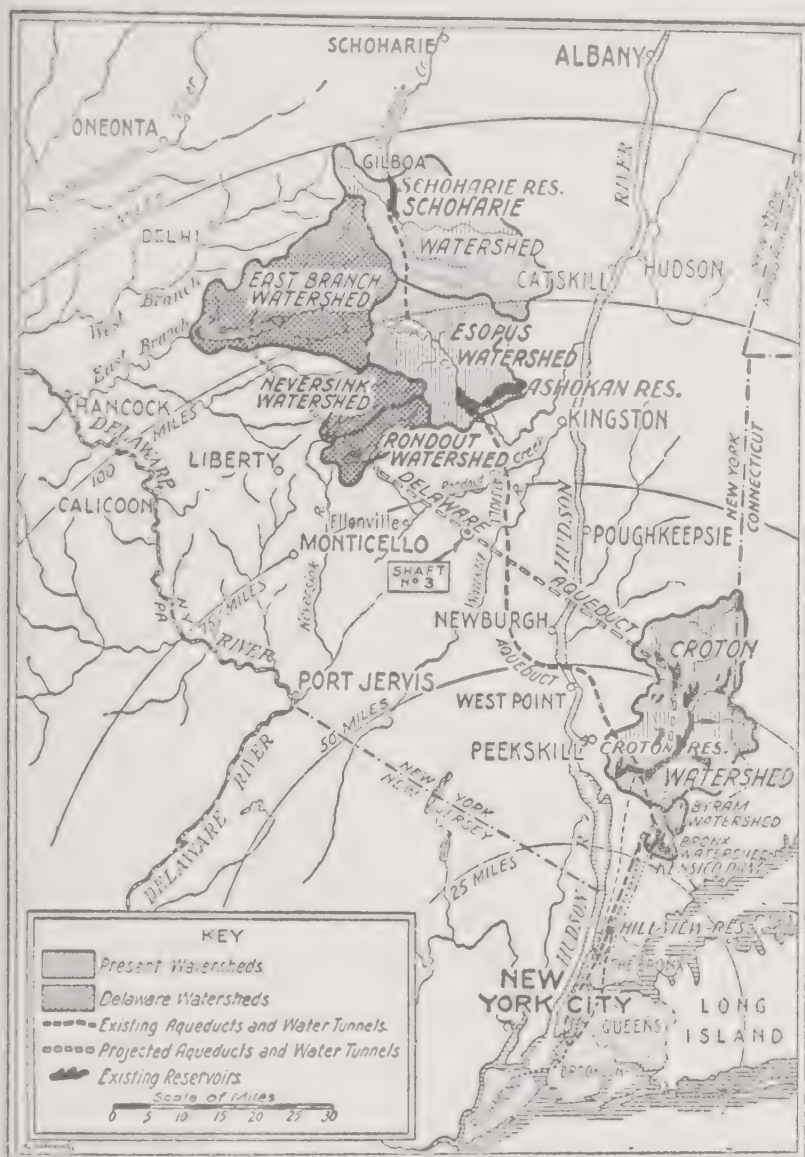


FIGURE 81a.—The sources of supply of potable water for the City of New York (as planned in 1937). [By permission.]

For New York City,³ just under 1 billion gallons per day is supplied from four different sources; surface water from the Catskill system (Asho-

From data kindly supplied by the Bureau of Water Supply, New York City.

kan and other basins), the Croton system, and the Long Island system. A comparatively small portion (50 mgd.) comes from wells. The main source is the Ashokan system; a tunnel brings it from the west side of Hudson, under the river, to the Kensico reservoir, and from there south through Westchester County to the city line, a distance of 92 miles.

Sufficient chlorine is injected, at a number of points (50), to produce a constant residual chlorine varying from 0.05 ppm. in water going directly into the distribution system, to 0.10 ppm. at the more distant stations. The actual dosage varies from $\frac{1}{2}$ pound to 5 pounds per million gallons.

To control a colloidal clay turbidity occurring at intervals in the Catskill system, the water is treated in the aqueduct between Ashokan and Kensico reservoir with soda ash and filter alum: soda ash from 0.25 to 0.50 grain per gallon, alum from 0.50 to 1.0 grain per gallon, according to the turbidity which varies from 10 to 100 ppm. The alum floc and turbidity is settled out in the Kensico reservoir. An efficiency of 95 per cent removal of turbidity has been attained.

The Catskill water is aerated at both Ashokan and Kensico by projecting it vertically into the air through about 1600 nozzles. The necessary height is furnished by gravity.

Copper sulfate, an algicide, is applied at the Ashokan basin by dragging crystals in burlap bags suspended from a rowboat or motor launch, traveling back and forth over the surface.⁴ It is also applied by dry feed at various points; at Muscoot Dam, Croton Lake, it has been fed in continuously several years by pumping a dilute solution through a 1000-foot pipe about one foot under the surface with nozzles every two feet. In 1931, about 100 tons in all were used.

The water is distributed to the five boroughs by a circular tunnel in the rock below; the tunnel is 15 feet in diameter in the northern part of the system and 11 feet near its end; the tunnel lies 200 to 750 feet below street.

Average analyses of the water supply from the various sources are given in Table 27.

General Remarks on Water Purification. For municipal purposes, the factor of safety to health is the controlling one, so that the purification is really a sterilization—a destruction of bacterial life—with improvements in taste and color incidental. The question of hardness does not matter very much. For sterilization, chlorine gas is almost universally used, but other agents are: bleach, ammonia gas and chlorine gas combined; ultraviolet rays from mercury-arc lamps, quartz-enclosed. If turbidity is present it may be removed by the action of a coagulant; a high proportion of bacteria is removed, incidental to this clarification. This operation precedes chlorination.

When a coagulant is needed, for the removal of turbidity and suspended matter, aluminum sulfate is almost the universal choice; it is called "filter alum." The amount of filter alum required depends upon the turbidity, and

⁴ "Control of microscopic organisms in public water supplies, with particular reference to New York City," Frank E. Hale, *J. New England Water Works Assoc.*, 44, 361 (1930).

Table 27.—Average analyses of Catskill, Croton, and Long Island water supplies for the City of New York, for the year 1941*

	Catskill	Croton	Long Island
Turbidity (ppm. silica)	2	2	2
Color (ppm. platinum)	5	8	7
Odor	1v	1v	1v
Albuminoid ammonia (ppm. nitrogen).....	.088	.111	.077
Free ammonia (ppm. nitrogen)060	.043	.108
Nitrite (ppm. nitrogen)001	.001	.000
Nitrate (ppm. nitrogen)09	.16	2.67
Total solids (ppm.)	40	76	100
Dissolved solids (ppm.)	29	55	61
Chlorine as chlorides (ppm.)	1.7	3.2	9.3
Hardness (ppm. CaCO ₃)	19	44	35
Alkalinity (ppm. CaCO ₃)	11	34	10
Iron (ppm.)13	.13	.38
Hydrogen ion (pH)	6.9	7.2	6.0
Bacterial count, per cc. (37° C. Agar)	5	17	6.0
<i>B. coli</i> per 10 cc.03	.02	.05
Microscopical: total organisms, standard units per cc.	105	75	60
Amorphous matter, st. u. per cc.	255	280	580

* Source of samples: Catskill: shaft No. 16-A, Brooklyn; Croton: 9th avenue and 20th street, Manhattan; Long Island: Ridgewood pumping station, Brooklyn. (By courtesy of Department of Water, Gas and Electricity, Patrick Quilty, Commissioner, and Frank E. Hale, Director of Laboratories, City of New York.)

* All municipal water analyses record *Bacterium coli* separately and in addition to the complete bacterial count, because it is an indicator of the presence of animal or human waste in the water.

a considerable degree upon the temperature of the water, the colder water requiring more.⁵

Salts of the alkali metals and alkaline earths are present in most waters: the most common are calcium, magnesium, sodium and potassium, combined with the bicarbonate, carbonate, sulfate, chloride, nitrate, and nitrite ions. The alkalinity is usually sufficient to precipitate aluminum hydroxide from dissolved alum; but if it is not, an appropriate amount of milk of lime or soda ash is added.

The presence of 0.1 to 0.2 ppm. of iron is enough to be troublesome, especially in the staining of fabrics and plumbing fixtures. It also stimulates the growth of *Crenothrix*, a thread-like organism which decomposes iron and manganese compounds with the formation of their hydroxides, and gives the water a bad taste and odor. When iron is present, it is generally in the form of ferrous carbonate or bicarbonate. On exposure to the air these compounds oxidize, and insoluble ferric hydroxide is formed. As small a quantity of iron as 2 ppm. forms a bulky and unsightly precipitate, sufficient to plug pipes. Iron may be removed by aeration followed by sedimentation. Aeration is accomplished by spraying the water into the air, or causing it to cascade over a bed of coarse material. Other aims in aeration: noxious gases are able to escape, certain small organisms are destroyed, and taste is improved. Algae frequently give rise to the formation of a green scum in reservoirs and water mains which must be removed mechanically, or better, prevented from forming by a chemical agent. Of the many acids recommended, copper sulfate is the cheapest and most efficient.

* See curves showing relation between amounts of coagulant, temperature of water, and turbidity of untreated and raw water, "Water Purification," Joseph W. Ellis, New York, McGraw-Hill Book Co. 1928, 2d ed., p. 412.

The removal of phenol from gas and coke plant wastes which in reach the municipal supply is described in Chapter 14.

THE USE OF AMMONIA IN WATER PURIFICATION

In a few localities since 1918, in a fast growing number since 1919, ammonia is injected into municipal water supplies in addition to chlorine bleach. This use of ammonia serves to lower the amount of chlorine bleach needed for bacteria removal; it decreases the taste due to chlorine phenolic bodies, and successfully prevents slime formation in mill waters, power plant condensers. It was pointed out by Rideal (in 1910) that a hypochlorite solution containing 1 per cent available chlorine had a ph number of 2.18, while the same solution mixed with one equivalent ammonia had the coefficient 6.36, more than three times greater. Chlorine and ammonia form chiefly monochloramine, NH_2Cl , which is a powerful bactericide, yet less energetic chemically than chlorine, so that it does not attack such organic molecules as phenol. The ratio of ammonia to chlorine should be as 1 is to 4; when necessary, as 2 is to 3. The reaction is: $2\text{NH}_3 + \text{Cl}_2 = \text{NH}_2\text{Cl}(\text{chloramine}) + \text{NH}_4\text{Cl}$.

A striking success was scored by the combined ammonia and chlorine system at the Tampa (Florida) water works. The average dose before adoption of the new system was 16 pounds of chlorine per million gallons. This left a chlorine residue of 0.25 ppm. In the new system, 5.6 pounds of chlorine and 1.9 pounds of ammonia for the same volume were used. This left an average residue of 0.35 ppm., higher than previous and enough to eliminate aftergrowth altogether. The cost is \$0.94 against \$1.54 by chlorine alone. A swampy odor and taste have been eliminated.

The water in swimming pools is sterilized by passing it over a quartz mercury-arc lamp, whose short rays (ultraviolet) are effective in reducing the bacteria count. The combined ammonia-chlorine purification has been applied in a number of swimming pools⁶ with satisfactory results. The method most in use, however, is the application of chlorine.

WATER FOR INDUSTRIAL PURPOSES

In the further consideration of the supply of water for the industries, a number of requirements must be met. The most important is that the water should be cheap.

Over half the water used in chemical plants is for cooling; it would be economically impossible to purchase city water, assuming that the capacity of the city system would be adequate. The composition for cooling water is of no great importance; its function is to carry away heat, by warming by evaporation. Water fed to steel jackets forming the walls of a combustion blast furnace; water flowing around a Cellarius vessel through which hydrogen chloride passes, and cooling water flowing through the jacket of a three stage compressor, illustrate the first; a trickle of water over an ammonia condenser, the second.

⁶ "Precautions needed in the ammonia-chlorine treatment of swimming pools," Lyle L. Jenne and Henry R. Weisford, *Ind. Eng. Chem.*, 23, 32 (1931).

The water is drawn from a near-by river or lake, and passed through a pressure type sand filter to remove any suspended matter which might clog pipes and valves. A fish trap protects the pump, which may be a Commercial blower, or a centrifugal pump. The sand filter is similar in construction and operation to the gravity type described, except that it is contained in a cylindrical steel shell, either horizontal or vertical. The water enters at the top and leaves at the bottom, through a riser which brings the water to an elevated tank, from which it is fed to the parts to be cooled by gravity. The capacity of the pressure sand filters vary with the size, from 100 to 36,000 gallons per hour.

If available river water is not cool enough, artesian wells are driven; these frequently have maintained a flow of water of 54° F. (12.2° C.) the year round.

Filtering may be dispensed with, if the piping is short and accessible; rackishness does not matter if the vessels to be cooled are stoneware. In the case of cast iron and steel, an occasional replacement because of corrosion by the cooling water may be preferable to an elaborate installation for treating it.

Another considerable volume of water is used in the chemical plants for solution and dilution; as a rule, a reasonably pure river water is all that is needed.

These water requirements are usually readily met, because chemical plants are purposely located near an abundant supply of water, to be had at low pumping costs.

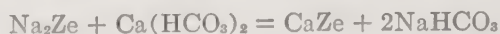
Water Softening. In dye application plants, in commercial and hospital laundries, in rayon plants, and others, the water used in processing must meet more rigid requirements. As a rule, it must be soft. If the only available supply of water is hard, the water must be treated to remove dissolved calcium and magnesium salts. This is done by means of (1) lime and soda ash addition, followed by settling and filtering, or (2) trisodium phosphate addition, or (3) contact with zeolites. The softening of water for use in steam boilers has been discussed in the preceding chapter; some supplementary remarks will be given here.

(1) The reason for combining the lime with the soda ash treatment is as follows: The carbonate hardness (old temporary hardness) leads to the reactions: $\text{Ca}(\text{HCO}_3)_2 + \text{Ca}(\text{OH})_2 = 2\text{CaCO}_3 + 2\text{H}_2\text{O}$, and $\text{Mg}(\text{HCO}_3)_2 + \text{Ca}(\text{OH})_2 = \text{MgCO}_3 + \text{CaCO}_3 + 2\text{H}_2\text{O}$. The magnesium carbonate is fairly soluble (100 ppm.) and requires an excess of lime: $\text{MgCO}_3 + \text{Ca}(\text{OH})_2 = \text{Mg}(\text{OH})_2 + \text{CaCO}_3$. The magnesium hydroxide is insoluble, as is the calcium carbonate, and both settle out. If magnesium chloride is present, the reaction $\text{MgCl}_2 + \text{Ca}(\text{OH})_2 = \text{Mg}(\text{OH})_2 + \text{CaCl}_2$ takes place, and although magnesium hydroxide precipitates, an equivalent amount of calcium chloride is in solution; no true softening has been achieved. Accordingly, sufficient soda ash is added to precipitate the calcium chloride, as well as any calcium chloride, nitrate, or sulfate originally present, which remain unattacked by lime: $\text{CaCl}_2 + \text{Na}_2\text{CO}_3 = \text{CaCO}_3 + 2\text{NaCl}$, or $\text{CaSO}_4 + \text{Na}_2\text{CO}_3 = \text{CaCO}_3 + \text{Na}_2\text{SO}_4$. All the dissolved salts mentioned in this paragraph except the bicarbonates make up the non-carbonate hardness;

only the calcium sulfate is scale-forming, but any of the others will bi soap or dyes. It should be understood that the magnesium sulfate undergoes the same reactions as the chloride.⁷

It is clear that the amount of lime and soda ash will be determined by the analysis of the water, supplemented by the actual results of the treatment. A large installation for softening would resemble a municipal filtration plant. On a smaller scale, two tanks may be used; in one, the raw water receives the dosage of chemicals, and after stirring, is left to settle. In the meantime, the other may be drawn off, the comparatively clear water only passing to the sand filter, while the main part of the precipitate is run to the sewer. Hot water is frequently employed; the treatment and settling takes place in a large tank; here again, only the clear supernatant water passes to the filter. In the case of hot water, the action and the settling of the precipitate are more rapid. In an hour, an effluent with only 25 ppm is obtained. The application of trisodium phosphate, (2), an alkaline substance, is similar.

(3) In contact with zeolite,⁸ the following reaction takes place:



The symbol Ze stands for the zeolite radical: $2\text{SiO}_2 \cdot \text{Al}_2\text{O}_3 \cdot \text{Na}_2\text{O}$, which is now written Na_2Ze . This is preferable, because a zeolite containing molecules of SiO_2 is not suitable, and must be replaced in practice with zeolites containing from 5 to 13 molecules of SiO_2 . The water gives up its calcium and receives an equivalent amount of sodium. After 6 to 8 hours the flow of raw water is stopped, and the container filled with brine (saturated sodium chloride solution). (See Fig. 82.) The reaction



takes place, in a period which was originally 6 hours. After that time, the salt solution is drawn off, the vessel rinsed, and the raw water sent in. The "hardness" in the form of calcium and magnesium chlorides passes out with the salt solution. Improvements in the manufacture of zeolite have led to the rapid type of exchange material, the gel type or porous type; the softening action is more rapid, and the regeneration also (30 minutes). A successful commercial zeolite is made from New Jersey greensand (glauconite), by special treatment. The apparatus for softening resembles the pressure sand filters, with zeolite in grain form instead of the sand. It has been found that upflow as well as downflow may be practiced; with upflow a greater softening capacity is reached.⁹

The softening capacity for greensand type zeolites is from 2,800 to 5,000 grains (as CaCO_3) per cubic foot of zeolite (weight 85 to 92 lbs. per cubic foot); for the synthetic types, up to 10,000 grains per cubic foot of zeolite.

⁷ For a more detailed treatment, see the chapter on "Lime and soda process" in "The chemistry of water and sewage treatment," A. M. Buswell, New York, Chemical Catalog Co., Inc. (Rembert Publishing Corp.), 1928.

⁸ For the manufacture of these, see U. S. Patents 1,343,927 and 1,304,206.

⁹ "Recent developments in zeolite softening," A. S. Behrman, *Ind. Eng. Chem.*, 19, 445 (1927). "Zeolites, mining, processing, manufacture, and uses," Eskel Nordell, 9th annual Michigan Conference on water purification, Bull. 61, Jan., 1935.

weight 50 to 60 lbs. per cubic foot). The effluent may be as low as 5 ppm in hardness.

A plant which draws its own water from a river would send a portion of it through the zeolite softeners or lime-soda ash system, for use in its boilers, or in the washing, dissolving or diluting operations which call for soft water. The greater part of the water supply would serve untreated.

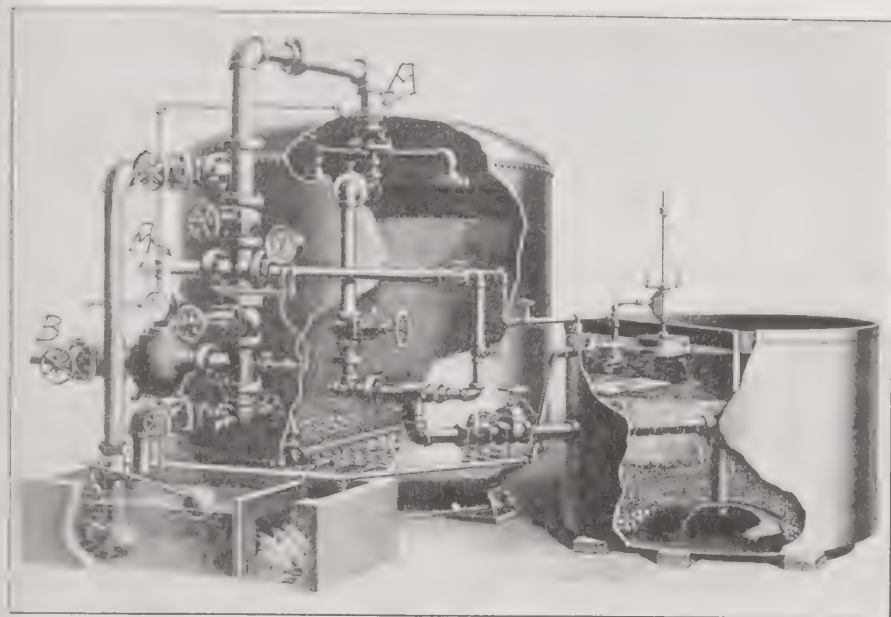


FIGURE 82.—Permutit vertical zeolite water softener, pressure, downflow type, showing the zeolite bed in the softener. Raw water inlet A, treated water outlet B, brine tank with bed of salt, and brine pipe with ejector from bottom of brine tank to the distributors at top of zeolite tank. (Courtesy of The Permutit Co., New York.)

Among the new zeolite developments there should be mentioned Zeo-Karb, a high-capacity carbonaceous zeolite. It is made from coal, lignite or wood, by treatment with oleum, chlorsulfonic acid or other agents, then washed, "stabilized," and screened to size. Zeo-Karb can function in the sodium zeolite cycle, taking up calcium and magnesium from the water and giving it sodium in exchange; the revivification is by treatment with salt solution. But it may also function in the hydrogen zeolite cycle, in which the metal ions, calcium, magnesium and sodium, leave the water to be replaced by hydrogen ions; the revivification is then by dilute acid treatment. In waters containing calcium bicarbonate, which are very common, the hydrogen zeolite removes the calcium ion, and produces H_2CO_3 , which may be driven out in a degasifier, resulting in a complete removal of the original bicarbonate.*

Synthetic resins exhibit ion-exchange properties, for example, phenol-

* "Carbonaceous zeolites, an advance in boiler-feedwater conditioning," by Howard L. Tiger, *Trans. S.T.M.*, pp. 315-325, 1938.

formaldehyde, amine-formaldehyde, tannin-formaldehyde resins and others.

It might be well to enumerate the requirements of waters to be used in certain important industries. Boiler water should be as soft as possible to prevent incrustations on boiler plates and tubes. Water to be used in laundries should be relatively soft and free from iron and manganese. Paper mills require that a water should not contain iron, since this stains the paper, and an excess of calcium and magnesium is to be avoided because they tend to precipitate the rosin soaps which are used in sizing the paper. Water containing sulfates, alkali carbonates, nitrates, and bacteria must be avoided in sugar refineries if the sugar is to crystallize well, is not to become deliquescent, and not decomposed while standing in storage. Alcohol distilleries require a cool water containing few micro-organisms and relatively little sodium and magnesium chlorides. Bakeries require a potable water with a minimum of organic matter which might affect the action of yeast. Water to be used in dyeing should be free of iron, and contain little hardness in order to avoid the formation of insoluble lakes, which give impure shades and often spot the fabric. Wool and cotton mills require a very soft water in order that undue amounts of soap will not be wasted in washing the yarn. Viscose silk plants must have water absolutely free from copper. The soft beverage trade usually uses distilled water which has been sand filtered, chlorinated, and then filtered through activated carbon to remove tastes and odors; also, if the alkalinity is high, lime softening is practiced to reduce it.

"Heavy water," that is, water containing the heavy hydrogen isotope deuterium (mass 2) instead of hydrogen (mass 1), plays no rôle as yet in the industrial world.

SEWAGE DISPOSAL PLANTS

Methods for sewage disposal may be grouped into two classes, those without treatment, and those with treatment of the sewage. By sewage is meant any waste at all which is sent out of households and habitations of any kind, manufacturing plants, and city streets. Its composition varies according to origin, and in some cases special treatment may be required; in the present discussion will be limited to the more typical city wastes, in which putrefiable organic matter is carried away by a considerable amount of flushing water.

Of the methods in the first class, the disposal by discharge into a water course is an example, and is a case of disposal by dilution. It is extremely simple, and except for some screens to catch large and coarse objects, the apparatus is of no importance. If the flow of the water course is 7000 gallons per capita per day, disposal by dilution is acceptable.

In the second class, a distinction may be made between settling methods and complete digestion followed by settling and filtration.

Settling Methods. The raw sewage is admitted to a sedimentation tank in which the mud settles. The effluent is discharged into rivers or first filtered, then discharged, while the sediment passes to another tank where it

† "Synthetic resins as exchange adsorbents," by Robert J. Myers, John W. Eastes, and Frederick J. Myers, *Ind. Eng. Chem.*, 33, 697 (1941).

is dissolved or volatilized. After a period, it is pumped in slurry form to filter beds, which allow the water to flow off, while the now inoffensive mud remains behind. During the rotting period, micro-organisms grow, with the simultaneous evolution of gases, mostly methane and carbon dioxide. In some of the European installations, the gas is burned under a boiler.¹⁰

FIGURE 83.—Imhoff tank. Upper drawing, plan view of the tank, showing circulation. The flow through the tank is reversed periodically; direct flow is through gates 1, 4, 3, 7, and 9, with the others closed (solid arrows); reversed flow through 2, 8, to the tank, out through 4, 5, and 6, with the remainder closed (dotted arrows). Lower drawing, cross section; B, discharge for the sludge.



Imhoff Tank. Simplicity in construction and operation is secured by placing the sedimentation tank above the digestion tank, so that the sediment may be fed to the digestion tank by gravity. This is the principle of the well-known and popular Imhoff tank, illustrated in Figure 83. The retention time is about 2 hours.

The effluent from the Imhoff tank is chlorinated, and then sent to a river or stream. If another community is situated down river which draws

¹⁰ "Fachbuch der Stadt-Entwässerung." K. Imhoff, Munich and Berlin, R. Oldenbourg, 1932, p. 93.

FIGURE 83a.—View of a sewage disposal plant with four sedimentation tanks, four sludge digestion tanks and incinerator close by. The outfall from the four thickeners, visible at right of center between them, is chlorinated. (By permission.)



water from the river for municipal use, the up-river plant is required to send its effluent through trickle filters, in which it is sprayed into the atmosphere, falling on a gravel and sand filter, then only, after chlorination, reaching the river.

The Imhoff tank is well adapted to small and medium-size cities. It removes from 50 to 80 per cent of the total solids in the raw sewage.

Septic Tank. In the septic tank, the sediment is allowed to remain until it is rather well digested; it is really a sedimentation and digestion tank in one, and is cleaned only once a year. It has been adapted to fair-sized cities, and is in general use for single dwellings without sewer connections.

The Imhoff tank may be considered a perfected septic tank, in which anaerobic fermentation takes place undisturbed by the flow of the sewage proper.

The sewage disposal plant for the city of Worcester, Massachusetts (200,000 inhabitants), is an installation of Imhoff tanks on a grand scale. The plant is in sight of U. S. Highway No. 20. The functioning of the tanks is essentially like that of the smaller plant described. The raw sewage passes through the following divisions: grit chambers (2); screens (2); Imhoff tanks (12), each one of which is 32 feet deep, 50 by 50 feet in area, and divided into 4 parts; the direction of flow is reversed once a month; dosing tanks (8), for the distribution of the partially clarified sewage upon the trickling filters; trickling filters (4), on a lower level, and covering 13.68 acres; final settling tanks (4), to remove suspended matters from the effluent coming from the trickling filters. No chlorination is necessary; the effluent discharged into the Blackstone River may be kept indefinitely in a closed bottle at room temperature without developing any disagreeable or offensive odor. The quantity of sewage normally handled is between 17 and 24 mgd. The Imhoff tanks remove 56 to 62 per cent of the total solids. The appearance of the plant is that of a city park.

Power from the Sewage Gas. Reference has been made to European installations for producing power from the Imhoff tank gas. There is now an installation in America, in Durham, N. C., in which sewage gas from activated sludge tanks, in this case, becomes the fuel for gas engines which supply all the power required by the plant. Sludge from the primary settling basin, and skimmings from that same basin, are conditioned, by addition of lime generally, and the pH adjusted to 7.2. Pumped to closed digesters, this conditioned sludge, with the proper content of activated sludge, is digested at 82° F. (27.78° C.) for 30 days; the gas evolved during the digestion is discharged into a gas holder which exerts a pressure on the gas of 6 inches of water. The gas consists of methane and carbon dioxide, and its average B.t.u. over the year was 723 per cubic foot. The volume over the year (1935-1936) was 16 million cubic feet.^{10a}

ACTIVATED SLUDGE PROCESS

The activated sludge process "consists of the aeration of sewage in the presence of nitrifying and other organisms attached to the circulating

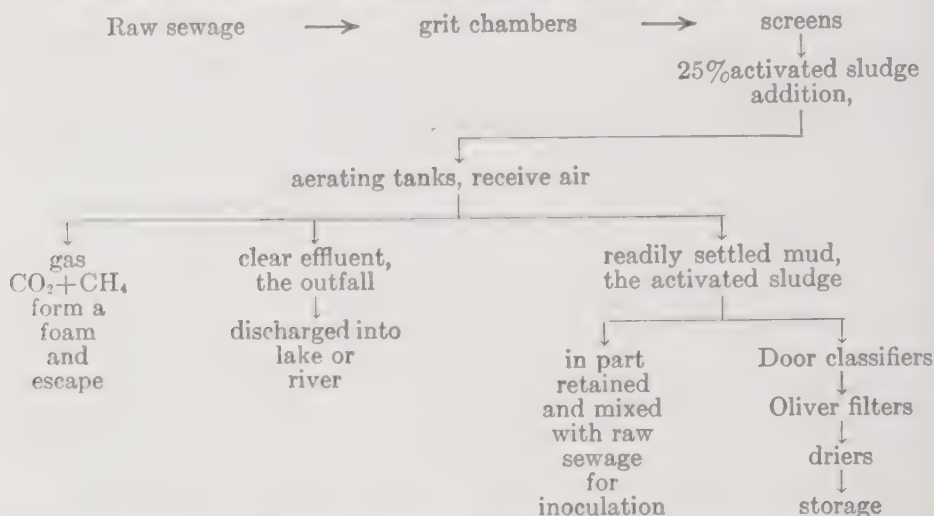
^{10a} "Sewage gas engines supply power for disposal plant at Durham, N. C.," Milton F. Merl, *Southwestern Power Journal*, 54, No. 12, 50 (1936).

sludge. It rests upon observations made in the course of a study of the effect upon fish life of water polluted to different degrees by sewage and other substances."¹¹

The process will be best explained in terms of an actual plant.

The Milwaukee Plant. The activated sludge process differs from the Imhoff tank and similar procedures in that it employs microbial growth under aerobic condition. Air is supplied, and the material is exposed to the open air in large, rather shallow tanks through which it travels slowly. Whatever action takes place in the digestion tanks of the Imhoff system

Simple Flow Sheet for the Activated Sludge Process of Sewage Disposal.



is anaerobic (that is, without oxygen). Another difference is that the digestion is made complete in the activated sludge process, whereas the rotting in the Imhoff system is partial.

A description of the Milwaukee disposal plant will permit the tracing of the sewage through the plant. (See Flow-Sheet above.) The raw sewage passes through grit chambers, then through fine screens, to reach an overflow chamber leading to the mixing channel. Here 25 per cent conditioned sludge enters and joins the raw sewage; this is now mixed sewage.

Filtered air is blown in, and the aerated mixed sewage passes to one of 12 double aeration chambers, open tanks 250 feet long by 85 feet wide. The mixed liquor is 15 feet in depth, and continues to receive air through diffuser plates located in the bottoms of the tanks. The volume of air blown in is just sufficient to produce complete digestion. A gas consisting of carbon dioxide and methane rises in sufficient volume to form a foam at the surface. Each aeration tank delivers its charge, after any one part of it has spent 6 hours in the tank, to a large sedimentation tank in which a Dorr classifier works; the clear, slightly colored effluent passes out to the lake and is called the outfall. Continuously also the classified mud is pumped in slurry form to a battery of 24 Oliver continuous filters with 14-foot drums, where it

¹¹ From a private communication from Dr. H. W. Clark, Chief Chemist, Mass. Dept. Public Health, to whom the observations are due.

dewatered. Animalia conveyors deliver the moist mud to rotary dewaterers ready for packing. It is used as fertilizer under the name *biogumite*, which analyzes 7 per cent nitrogen as NH_3 , and 2 per cent available phosphoric acid.

A portion of the sludge is conditioned by additional aeration and is used to inoculate the raw sewage.



FIGURE 84—Vorticella attached to sludge particles (100 \times); one of the protozoa in activated sludge. (Courtesy of Mr. Robert Cramer, Consulting Engineer, Milwaukee, Wis.)

The plant treats on the average 85 million gallons per day of a strong industrial sewage averaging close to 300 ppm. suspended solids.

A recent study¹² on the conditions necessary for the clarification of sewage as obtained in the activated sludge process indicates that there must be (1) aerobic bacterial life, (2) protozoa, and (3) oxygen in solution. The protozoa are living organisms, among which there may be mentioned the vorticella which is attached to a sludge particle by a stem. (See Figure 84).

The process of clarification from the colloidal standpoint consists partly

¹² "The rôle of protozoa in activated sludge," Robert Cramer, *Ind. Eng. Chem.*, 23, 309 (1931).

in the assimilation of matter in the colloidal state (albumen, mucin, protein, algal matter) and of dissolved organic bodies by the protozoa, bacteria, partly in their oxidation, due also to the presence and activity of the organisms. Because of the colloiddally protective function of albuminous matter and of dissolved organic substances on the suspended solids, the destruction of a small amount of the protectants permits the re-settling of a relatively large amount of solids.

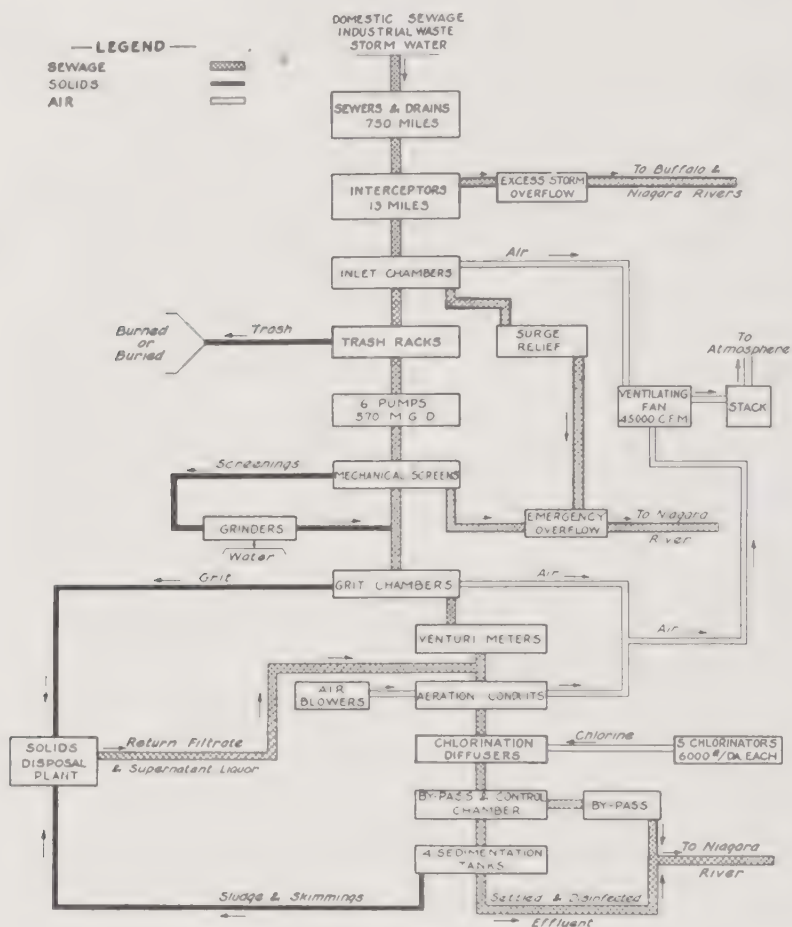


FIGURE 84a.—Flow sheet for sewage treatment in Buffalo Sewage Treatment Works. (By permission.)

A sewage disposal plant may be of still another type. The sewage is collected in preliminary tanks where first coarse matter, then sand, is removed. Suspended matter is next settled and thickened in standard thickeners, called sedimentation tanks which deliver over the edge clear water, and at bottom center the thickened sludge. The clear out is generally chlorinated. The thickened sludge is "digested," then filtered, dried, and burned; the gas generated during digestion is used as a fuel to raise steam. The Buffalo installation is such a plant.

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Until recently, the possession of coal fields was needed to insure security and industrial prosperity to a nation; with the advances in water power and the discovery of petroleum in certain coal-poor states, a partial independence of coal has resulted. Nevertheless, as a source of illuminating gases, dyes, and certain explosives, coal remained for a while without substitute. This is no longer so; benzene is made in huge quantities by pyrolysis, followed by polymerization, from petroleum gases and natural gas; dyes and explosives may rest on this source. Coal therefore seemed neatly shunted down as to its industrial irreplacableness. Once again the wheel turns and as a source of motor spirits by hydrogenation, coal again assumes front rank position, to become a comfort to the nations which possess it. Ammonia had its source in coal, forty years ago; the greatly increased amounts of ammonia now marketed and consumed are made synthetically from atmospheric nitrogen, a store available to all. Thus does modern science offer compensations to nations not favored by a full list of natural resources.

Chapter 14

The Distillation of Coal for Gas, Coke, Tar, and Ammonia

The chief use of coal is as a fuel, as described in Chapter 12; but a high use (economically) can be made of this material, or at least certain grades of it, by separating from it those portions which may be used in other, more specific processes, and burning only that portion of the coal which cannot be so used. Also, it may be transformed into other forms of fuel, more valuable merely because of their greater convenience of application and transportation. The processes used are all destructive distillations, performed in the absence of air.

Coke which is made from the proper mixture of coals and heated long enough is a hard, strong material, the "metallurgical coke" used in blast furnaces. It is made by distilling, or coking, bituminous coal, in beehive ovens, in retorts, or in the by-product coke ovens of more recent developments. In 1940, 57,072,134 tons (2000 pounds) of coke were produced; this is a high figure, but the great need of metallurgical coke for war purposes will bring about still further increases. Also, the same need is bringing back the outmoded beehive oven. Until 1889, all coke was beehive coke and only gradually since then has the original 100 per cent decreased. The by-product oven coke became acceptable to the metallurgical trade, and reached 2.61 per cent in 1935; in 1940, it was twice that—5.3 per cent.

Of the total 1940 production, 75 per cent was metallurgical coke, which brought \$4.40 a ton.*

In the beehive process, coke is the sole product; a part of the volatile matter is lost outright; another part serves merely as fuel. In the by-product installations the volatile part is collected; the combustible gas-

* All figures from Minerals Yearbook for 1940.

filled from ammonia, tar, and vapors such as benzene, which are all by-passed and utilized. The yield of coke is higher in the modern oven; the average yield in 1940 was 70.53 per cent of the coal charged, in the by-product oven, and only 63.66 per cent in the beehive; this is a further argument, at least in peace time, against the beehive oven.*

FIGURE 86.—The Woodall-Duckham vertical continuous retort (left). The gas passes out by an offtake situated just in front of the coal magazine. [Courtesy of Jerome J. Morgan, publisher, Maplewood, N. J., and The Isbell-Porter Company, Newark, N. J.]

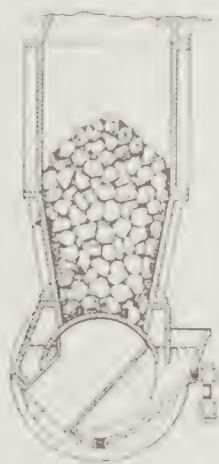
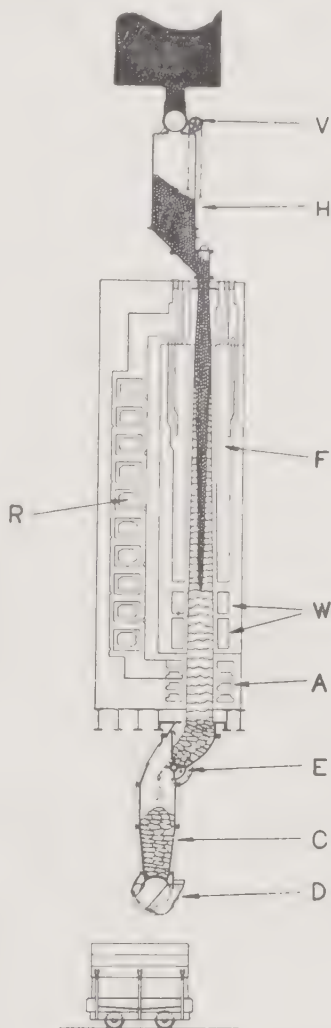


FIGURE 85.—Water-sealed gas-tight door (above). For discharging, the curved steel sheet just under the coke is rotated to the right and down, out of the way. [Courtesy of Jerome J. Morgan, publisher, Maplewood, N. J., and The Isbell-Porter Company, Newark, N. J.]



In municipal plants, coal is distilled in retorts, primarily for its gas. Originally, the coke produced was dumped onto the grates, to furnish the heat to the retorts above; but today the coke is generally sold for domestic use, and the heat required for the retorts is obtained by means of producer gas. In modern plants, the retorts are vertical, and circular or rectangular in cross-section.¹ The operation of coking is continuous; coal enters at the top by gravity; coke is withdrawn at the base, periodically, through a

* The Glover and West, and the Woodall-Duckham.

water-sealed valve. The Woodall-Duckham vertical continuous retort will serve as an example. It is 25 feet high, about 4 feet by 8 inches at the top, and 4 feet by 20 inches at the base; hence it is a narrow chamber, wide at the base, so that the coke works down by its own weight. It is built of silica bricks, and is heated by burning producer gas with preheated air flues provided in the wall. The temperature at the wall is 2500°F. (1370°C.), while the temperature of the coke itself is $1300\text{--}1400^{\circ}\text{F.}$ ($704\text{--}760^{\circ}\text{C.}$). The through-put of coal is $7\frac{1}{2}$ tons per day. Steam (10 per cent by weight based on the coal) is blown into the retort at a constant rate, so that a mixture of water gas and coal gas is the product. Per ton of coal, about 12,500 cu. ft. of gas are collected. Four retorts form a bench; 5 benches on each side of an aisle form an average unit.

The coke is worked out by a slow-moving helical grate, and reaches a quenching box, from which it is discharged by a hand-operated semi-butterfly valve.

The gas is purified from tar and ammonia, which are recovered, so that the plants belong to the by-product class. For small installations, they are very satisfactory; for large cities, the by-product coke ovens such as those of Otto, Semet-Solvay, and Koppers are more economical, in spite of a high first cost.

BY-PRODUCT COKE OVENS

For modern plants of large capacity, the oven is a narrow vertical chamber with silica-brick walls; the chamber is 28 to 39 feet long, 14 feet high, and has an average width of 14 to 18 inches. It is wider at one end (19 inches) than at the other (17 inches), in order to prevent jamming of the coke when discharging. Heat is supplied by burning gas on the outside of the chamber walls. A number of ovens (such as 60) form a block; the operation is intermittent per oven, but continuous for the block. The period of heating varies; an average is 17 hours.² The temperature in the flues, that is, at the outer side of the chamber wall, lies between 2150° and 2550°F. (1177° and 1400°C.); the temperature of the coal within the chamber is less, perhaps 1800°F. as maximum (982°C.) would be a fair average. These are the temperatures found in general practice, which is termed high-temperature carbonization, in contrast to many proposals for working at lower temperatures, referred to as low-temperature carbonization processes; these are discussed briefly further on. Generally the air for combustion is preheated, the gas is not. The outgoing gases furnish heat in regenerating chambers, of which there are, in one type of construction, two per oven. The direction of the air and of the fire gases is reversed every 10 or 20 minutes; a scheme for reversing is illustrated in Chapter 11. At the end of the distillation period, the red-hot mass of coke is pushed out of the oven in a single stroke of a ram, in the short space of 3 minutes; the oven is elevated so that the coke may be made to fall into a special car on railway tracks. The car is pulled to the quench hood, and there quenched by water. It is then dumped onto a sloping platform which leads to be-

² Coke oven engineers speak of "inch-hours," obtained by dividing the period of coking in hours by the width of the oven in inches; hence it is the number of hours per inch. The effort is to reduce

conveyors; those bring the coke to screens, chutes, and railway cars for shipment. The oven charge is 11 tons of coal, or more.

In the arch forming the roof of the oven, 4 charging holes are provided, with a fifth opening for the escape of the gases; the latter opening forms a cast-iron gaseous neck, which reaches into a horizontal steel trough running the length of the block, the "hydraulic main." The gas from all retorts is collected in this main and conveyed by extensions to the coolers, scrubbers, and meters; the liquid in the main (tar), overlaid by an impure ammoniacal water solution, serves as a seal to each retort, so that while the gas is being discharged, the gas does not escape, nor does air enter. The

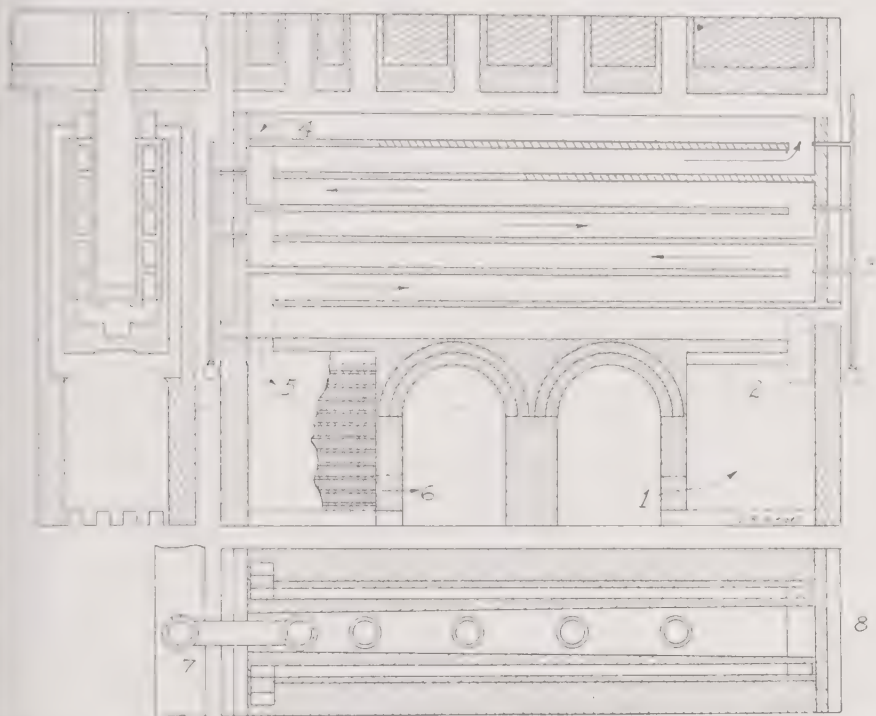


FIG. 87.—*Upper right*, vertical cross-section, lengthwise, through the Semet-Solvay by-product coke oven, showing the heating flues. Air from tunnel 1 enters the hot checkerwork in regenerator 2, and passes along the flues and upward, burning the gas which enters through burners 3; the fire gases descend at 4 through a vertical channel to regenerator 5, and to the stack through tunnel 6. *Upper left*, vertical cross-section, crosswise, showing flues and oven proper. *Lower right*, horizontal cross-section showing width of the flues and taper of oven, also the four charging holes and the hydraulic main connection at 7; the ram enters under 7, the coke drops off at 8. For dimensions, see text.

front and back of the oven are closed by cast-iron doors lined with silica bricks. When reset after discharge, the doors are luted with mud to make them gas-tight.

The coal is charged from a special car traveling on tracks laid on the top of the ovens. The coal is carefully chosen; nearly always a mixture of two or more kinds is used, to obtain a coke which will be suitable for

metallurgical purposes. The mixture may be 20 per cent of a low-volatile coal (16-18 per cent volatiles), and the rest a higher-volatile coal (30-35 per cent volatiles) with coking properties. The coal is crushed by rolls followed by a swing-hammer mill³; it is conveyed to a bin sufficiently elevated so that the traveling charging car may be loaded by gravity.

Dry Quenching of Coke. The heat in the coke and hot gases represents 70 per cent of the applied heat. When the hot coke is quenched with a stream of water, as is the custom, its sensible heat is wasted. Attempts have been made to substitute "dry quenching," by circulating an inert gas over the coke and under a boiler; in one trial which has been reported a recovery of 70 to 75 per cent was made.

Cooling and Purifying the Gas. Assuming that the gas is to be sold to a municipality, it must pass certain tests of purity, and on burning must furnish 537 B.t.u.^{4a} per cubic foot. Formerly a candle-power requirement was also made, usually 18 candle power; the tendency is to abolish it because the gas flame alone is now rarely used for light. The purification leads to the collection of the by-products, tar and ammonia. The appreciable content of benzene and homologs would not need to be removed, but since the purpose of these ovens is to provide by-products, they are scrubbed out of the gas by oil. The removal of benzene lowers the candle power, but as this requirement is gradually disappearing, the gas remains salable. There is left in the gas a hydrogen sulfide impurity, which is removed by contact with wood shavings coated with lime and iron oxides, or by "liquid purification."

Coolers. The gas leaves the oven at rather moderate temperatures, for the greater part is evolved in the early stages of the coking. Some cooling takes place in the hydraulic main and its extensions leading to the cooler proper, so that it generally reaches the latter with a temperature of 170° F. (77° C.). The coolers consist of steel towers, with wooden grids; the gas comes into direct contact with the cooling liquid, a solution of ammonia which is itself cooled in pipes sprayed with water and recirculated. A gain in liquor occurs, for the gas holds less moisture cold than hot; this excess is sent to the ammonia still. The cooled gas is drawn by centrifugal exhausters from the cooler and pressed (warmed somewhat by the compression) past the baffles of a tar extraction box into the ammonia scrubbers.

Ammonia Extraction. *a. By scrubbers.* The gas rises in a steel box filled with grids, meeting a descending stream of weak ammonia liquor. From the first box it reaches a second, and a third, fourth and fifth, losing its ammonia. The liquor from the first tower (with respect to gas travel) is the strongest solution of ammonia; the fifth tower receives water, and its liquor is fed to the fourth tower, and so on. The cleaned gas passes to the benzene scrubbers. The ammonia is present in the form of ammonium hydroxide and of ammonium salts, sulfides, carbonates, and others.

b. By direct sulfate formation. This method renders subsequent distillation in a still unnecessary, and is therefore being adopted in all the

³ Chapter 44.

⁴ "Dry quenching of coke," D. W. Wilson, *Proc. Intern. Conf. Bituminous Coal, 2nd Conf.*, Pittsburgh, Pa., 2, 685 (1928).

^{4a} New York State Public Service Commission standard.

over installations. All the gas passes through a sulfuric acid solution, where the ammonia is retained and precipitated as ammonium sulfate. The slurry is continually pumped out (by a small steam-jet pump), the salt removed, and the mother liquor returned to the absorption box with additional sulfuric acid.

Benzene Recovery. After losing its ammonia, the gas travels upward through tall steel towers with grids, meeting a stream of "straw oil" which picks up the benzene and toluene from the gas. The charged oil is distilled, benzene collected and sold generally as motor spirits, and the free oil fed over again. As a rule, two towers work in series.

Purifying Boxes. The gas next enters the base of wide, low boxes which contain the iron oxide and lime impregnated on wood shavings; hydrogen sulfide is retained, forming iron sulfide. After a period, the mass must be exposed to the air, to be revived. A certain number of such exposures cause an accumulation of sulfur in the free state, and the mass may be used as a source of sulfur for sulfuric acid manufacture.⁵

FIGURE 88.—The Thomas meter for measuring the volume of gas flow; 1, heating coil; 2, thermometer for entering gas; 3, thermometer for outgoing gas; 4, galvanometer in the Wheatstone bridge *abcd*.



The Thomas Meter. There remain now only the metering of the finished gas and the testing of its heat value. The device generally adopted for metering is the Thomas meter (Fig. 88) in which a measured quantity of electrical current, sent into a resistance-wire heating coil, is so varied that a differential of 2° F. is maintained between the temperatures of the entering gas and the gas which has passed the coil. It is the variation in this heating current which forms the basis of the measurement. The temperatures of the gas affect the resistance of two nickel wire grids which form part of a Wheatstone bridge. With standard heating current and standard flow of gas, their resistance ratio is definite; any change in the flow disturbs the balance, and more or less current enters the heating grid by the aid of a small motor-driven regulator. The instrument is automatic and recording, and is graduated to read cubic feet directly.⁶

The Thomas Calorimeter. The heat content of the gas is measured continuously by the Thomas calorimeter, and the readings are recorded automatically on a chart indicating B.t.u. per cubic foot.⁶

Yield. The amounts of gas, coke, and other materials obtained from 1 ton of coal vary with the kind of coal used; as a guide, the following figures may be given:

⁵ The oxide is burned and the sulfur dioxide sent to chambers; carbon dioxide is evolved in the burning also, and tends to render the operation of the chamber very difficult.
⁶ From C. E. Howard Manufacturing Company, Milwaukee, Wis., publication T 4. The calorimeter reproduced in *Ind. Eng. Chem.*, 18, 1088 (1926).

1 ton of coal produces 10,000 to 11,000 cubic feet of gas
 1400 to 1500 pounds of coke
 10 gallons of tar
 18 to 30 pounds ammonium sulfate
 2.7 gallons motor spirits.

In 1940, the figures were: 10,900 cubic feet of gas, 8.79 gallons of tar, 22 pounds ammonium sulfate, 2.93 gallons crude light oil. (Bureau of Census).

A large portion of the tar is obtained from the hydraulic main, the liquid contents of which are allowed to overflow to the decanter, where the tar forms a lower layer, the ammoniacal liquor an upper layer.

In the Koppers oven, the flues in the chamber wall are vertical, and connected by cross-over channels to the flues in the opposite wall, where the gases descend and pass out to a regenerator. (See Fig. 89.) Other ovens are the Otto, the Wilputte, Foundation, Piette, and Roberts.

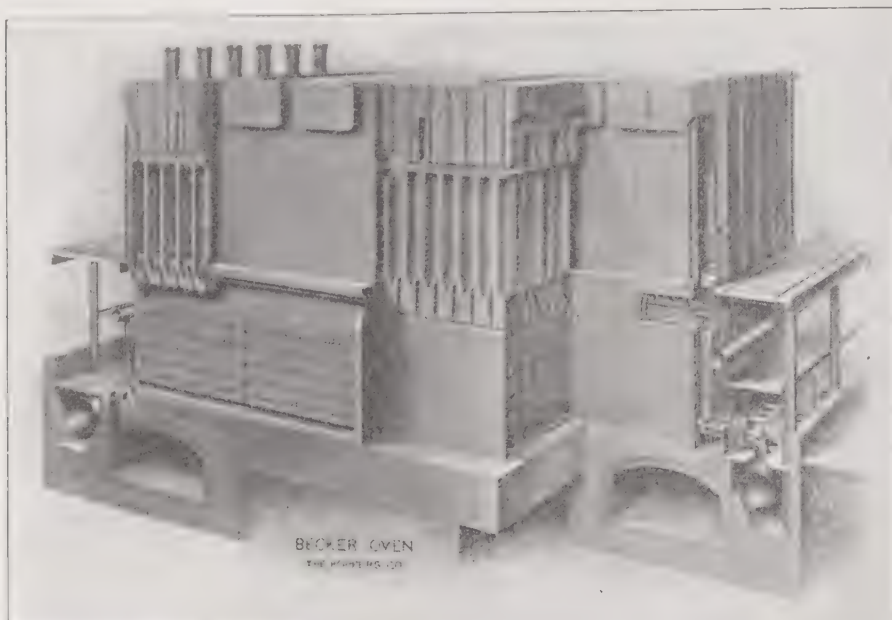


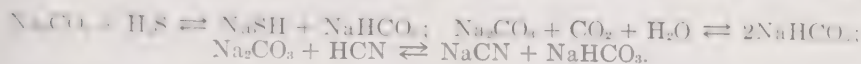
FIGURE 89.—A view of several vertical cross-sectional cuts through the Becker oven, showing: The two arched canals for air; the regenerators; the heating gas lines; the vertical flues with cross-overs; several ovens, and their charging inlets. The heating flames travel up on one side of oven, and down on the other, to enter the regenerator. As shown, the gas is not preheated in the coke oven structure. (Courtesy of the Koppers Construction Co., Pittsburgh, Pa.)

The combination of a water-gas plant ⁷ and a coke-oven gas plant is infrequent; the gases are sometimes mixed, or the water gas may be burned in the flues of the oven, thereby releasing the equivalent volume of coke-oven gas for sale.

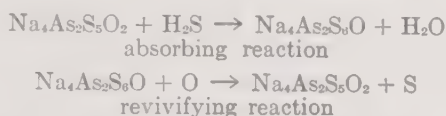
Liquid Purification. A new method for gas purification has been installed in several plants and has proved successful. It will replace the purifying boxes filled with the lime-iron oxide shavings, or both devices.

⁷ Chapter 15.

may be used, in the latter case, the oxide boxes, which receive the gas, already purified by the liquid process, would require refilling only at long intervals. The process is as follows:⁸ The gas passes upward in a tower of wooden staves, meeting a 2 to 5 per cent sodium carbonate solution. Hydrogen sulfide, carbon dioxide and hydrogen cyanide are retained in the water, while the clean gas passes on. The foul liquor is pumped to the top of a second tower, while hot, and meets a blast of air which travels upward, driving out hydrogen sulfide, hydrogen cyanide, and carbon dioxide. The reactions which take place are given below; they are reversible, and run to the right while the gas passes, but to the left while the air is blown in.



The gases passing out of the liquid purifying agent may be burned under small fire, to prevent a nuisance. Instead of driving out the gases, the sulfur may be recovered by the Thylox process,^{8a} in which hydrogen sulfide in the gas is retained and, in a subsequent step, transformed into elemental sulfur. A solution of sodium thioarsenate



retains the hydrogen sulfide; on blowing with air, part of the sulfur in the latter compound is liberated, and comes to the top of the solution; it is skimmed off and filter-pressed. In this change due to air, the first compound is reformed, and is ready for new absorption. Sulfur in this extremely finely divided form has proved to be a valuable fungicide.⁹

Triethanolamine (Chapter 25) has been used instead of soda ash in the liquid purification method for coke oven gas; after the absorbing liquid has taken up all the impurities it can hold, it is treated with steam which revivifies it, restoring it to its original state.¹⁰ Triethanolamine is a high-boiling liquid, strongly alkaline; it is used over and over again. Fig. 90 shows the apparatus employed.

Sodium Phenolate Gas Purification. Still another system of gas purification by means of liquids must be added to the list. It is the phenolate process, designed for the specific purpose of ridding refinery gas or natural gases of any hydrogen sulfide it may contain, an admixture which is frequently high. The absorbed hydrogen sulfide is liberated in the actifier, in concentrated form, and becomes the source of sulfur for the manufacture of sulfuric acid, displacing a corresponding tonnage of brimstone which otherwise would have to be bought. The phenolate process is timely, for by its means refinery and natural gases may be made pure enough for cracking and polymerization into synthetic gasoline.

⁸ U. S. Patents 1,389,980 and 1,390,087. See also the Petit process, in which a solution of potassium carbonate is employed, and essentially the same reactions take place; described on p. 537, "Modern House Practice," Alwynne Meade, London, Ernest Benn, Ltd., 1921.

^{8a} "Chemistry of the Thylox purification process," H. A. Gollmar, *Ind. Eng. Chem.*, 26, 130 (1934).

⁹ *Ind. Eng. Chem.*, 25, 364 (1933).

¹⁰ "Organic bases for gas purification," R. R. Bottoms, *Ind. Eng. Chem.*, 23, 501 (1931).

In the Koppers phenolate process^{10a} the refinery gas or natural gas rises in the plate column absorber, meeting a descending cold liquid, a solution of phenol in caustic. Essentially all the hydrogen sulfide present in the gas is absorbed (96 to 99.8 per cent). The charged solution passes through a heat exchanger, taking heat from the hot liquor leaving the absorber, and enters at the top of the latter, also a plate or bubble-cap tower only somewhat larger than the absorber. As the charged solution descends it meets steam rising from the lowest portion of the solution which lies in contact with a steam chest. The hydrogen sulfide with steam leaves

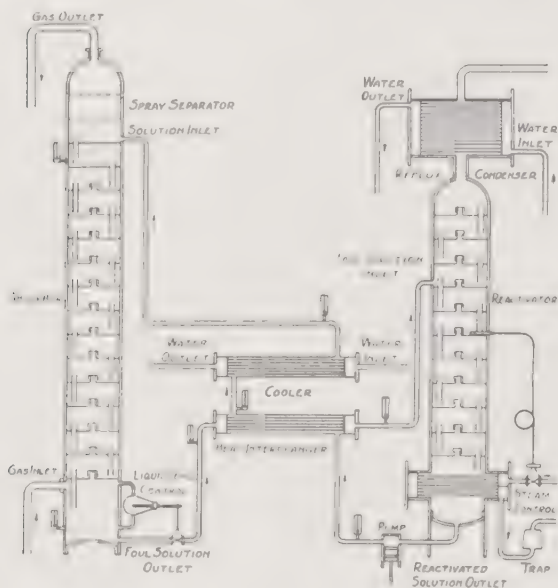


FIGURE 90.—Liquid purification of illuminating gas, using triethanolamine, with revivification of the absorbent by heat. (Courtesy of Mr. R. R. Bottoms, the Girdler Corporation, Louisville, Ky.)

actifier overhead, passes two dephlegmators, and thence to a burner for the production of sulfur dioxide. The liquor leaves the actifier hot, and free from hydrogen sulfide; it passes an exchanger and a cooler, and then enters the absorber, at the fourth plate from the top (12 plates in all). Fresh water is added continuously to the top tray of the absorber; the three top trays become, in effect, a water scrubber to retain entrained chemicals. At stated intervals (one week) chemicals lost to the system are replenished.

The high carrying capacity of this solution makes it possible to purify only 5 to 10 gallons of solution per 1000 cubic feet of sour gas; this is a low ratio, which means economy of installation and operation.

In general, the processes which recover sulfur as elemental sulfur operate on manufactured fuel gas, whereas those which recover hydrogen sulfide are applied to petroleum refinery still gases and natural gas; usually the latter gases are under high pressure. Production of elemental sulfur, mostly from the Thylox process, in 1940 totaled 3.942 long tons, valued at \$40.5 a ton. The hydrogen sulfide recovered is for the greater part made into sulfuric acid; the amount in 1940 so converted (again for the greater part

^{10a} "Koppers phenolate gas purification process for recovery of sulfur from natural and refinery gases," the Koppers Construction Company Pittsburgh, Pa.; also U. S. Patents 1,971,798, 2,002,208, 2,028,124, 2,028,125.

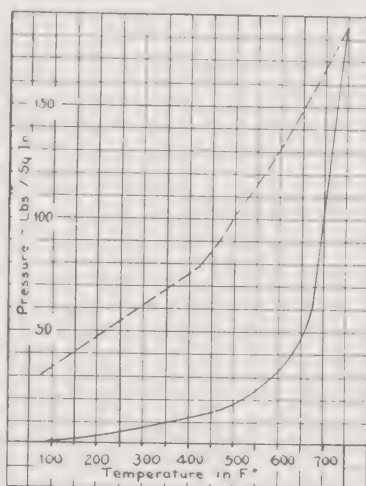
is equivalent to 15,918 tons of sulfur. The processes by which hydrogen sulfide as such is recovered¹⁰ are: the Carbated purification process, which uses mono- or methanolamine, the Shell phosphate process, in which the sorbing agent is an aqueous solution of impotassium phosphate (40 to 50 per cent by weight), the phenolate process, and others.

MODERN PRACTICE IN COAL-TAR DISTILLATION

In recent years, the distillation of coal tar has received much study and attention, and a number of improvements have been made.

The aim of the tar-distiller is to produce as much oil as possible (from which, then, more of the valuable constituents may be isolated), with a pitch having a high melting point, and at the same time to keep down the formation of free carbon. The higher the temperature, and the longer the tar is subjected to it, the more gas forms, and the less oil. The aims have been therefore to reduce the time of heating, to agitate the tar layers in con-

FIGURE 91.—The effect of heat on tar. Full curve, heating tar in autoclave; dotted curve, cooling same autoclave; the higher pressures are due to evolved gases.



act with the heating walls, or to operate in novel ways, avoiding all the old defects. A batch still is a steel vessel heated by an open fire; instead of heating only the lower half, all of it may be heated, reducing the recondensation on the cooler upper walls. The improvements include: modified batch stills, such as vacuum stills, stills with steam agitation, inert gas recirculation, and coke stills, in which the residual pitch is heated until only coke remains¹¹; pipe or tube stills, consisting of a coil of pipe set in a furnace, and through which the tar passes continuously; the coke-oven tar still, which is built on top of the coke-ovens, and employs lean coke-oven gas as source of heat.

As the heating of tar progresses, permanent gases are evolved, the free carbon content rises, and the melting point of the resulting pitch increases.

¹⁰ "Cleaning up refinery gases," report by staff member, *Chem. Met. Eng.*, 45, 417 (1938). "Recovery of sulfur from fuel gases," by Alfred R. Powell, *Ind. Eng. Chem.*, 31, 789 (1939), includes recent German processes.

¹¹ U. S. Patent 1,230,782.

The evolution of gases as measured by pressure is shown in Figure 91 it will be observed that changes are slow below 600° F. (315° C.), and rapid above 700° F. (371° C.). The increase of cracking as the temperature increased is evident. The free carbon increase is 15 per cent.

The improved recovery of oil in vacuum stills is shown in Table 28.¹

TABLE 28.—*Vacuum Stills vs. Atmospheric Stills.*

Stills	Temperature		Oil	Pitch Per cent	Free Carbon
	° C.	° F.			
Vacuum	330	626	56.6	42.5	28.8
Atmospheric	413	775	40.1	57.8	40.7

In the pitch from the atmospheric distillation the free carbon is 2.8 times that to be expected by the simple concentration of the free carbon present in the original tar; in the vacuum still the increase is 1.4 times. In stills with steam agitation, the improvement is similar.

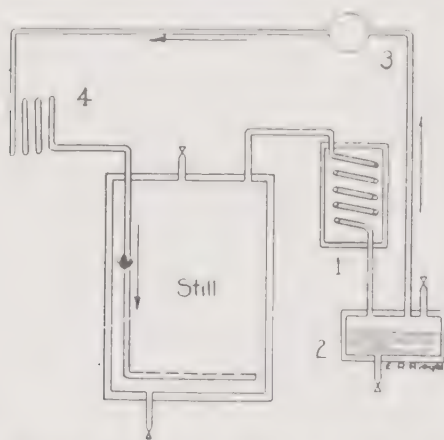


FIGURE 92.—Diagrammatic scheme for the inert gas recirculation process for distilling coal tar. 1, condenser; 2, receiver and separator, the gas passing out to pump 3; 4, heater.

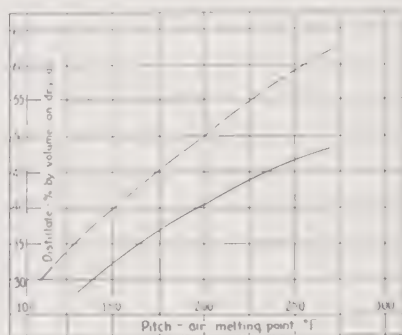


FIGURE 93.—Percentage distillate and corresponding pitch melting point from a tar still with inert gas circulation.

The inert gas circulation system¹³ (see Fig. 92) has the great advantage of being adaptable to any batch still; the improvement in amount of distillate and, at the same time, higher melting point of resulting pitch are well shown in Figure 93. At first, nitrogen or carbon dioxide was used, and the rate was 0.33 cu. ft. of gas per gallon of tar per minute for carbon dioxide.

TABLE 29.—*Inert Gas Circulation System vs. Atmospheric Distillation.*

System	Temperature		Pitch		Oil Per cent	Free carbon
	° C.	° F.	Per cent	M. pt.		
Atmospheric still	413	775	57.8	280° F. (138° C.)	40.1	40.7
Recirculated CO ₂	358	677	46.9	277° F. (136° C.)	52.6	29.0
Recirculated N ₂	331	628	46.4		52.0	27.2

¹² "The distillation of coal tar," by John M. Weiss, *J. Soc. Chem. Ind.*, 51, 219 (1932).

¹³ U. S. Patent 1,418,893; related schemes in U. S. Patent 1,800,224.

340 cu. ft. per gallon per minute for nitrogen. A sample of the results is given in Table 29.

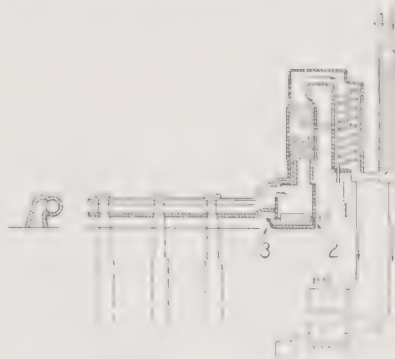
It was found that if air is recirculated, its oxygen is soon consumed, the residual gas is in effect inert. The method has been adapted to vessels of capacities varying up to 10,000 gallons.

A very recent improvement has been the placing of the distilling vessels just above the coke-ovens,⁴⁰ and utilizing the lean coke-oven gas as a source of heat. Only the sensible heat in such gas is used, and after contact with the tar, it rejoins the main flow of gas and yields its combustion heat elsewhere.

The cost for fuel is thus nil. Another advantage is that the crude tar need not be transported; any fractions which must be burned are so on the premises; only the parts for which there are orders are made near a shipping charge.

The procedure is indicated in Figure 94. The tar is preheated in the coil 1, and is delivered in spray form into the distilling tower, passing

FIGURE 94.—Tar still using the sensible heat of lean coke-oven gas. 1, entry for tar; 2, rotor roll to splash pitch; 3, draw-off for pitch; 4, entry for weak ammonia liquid; 5, outlet for cold gas.



ward. The hot coke-oven gas passes upward, volatilizing the oils, but leaving the pitch to pass down to the distilling main; in the latter a rotor works and splashes the pitch into the incoming gas. Periodically, pitch is withdrawn at 3. The gas leaves the tower laden with oil vapors; it cools the heavy oils while in contact with the coil bringing the new tar. Light oils are recovered in the final tower packed with rings, down which a cold ammoniacal water solution flows. The condensed light oil and water pass down to a separator, while the cleaned cool coke-oven gas leaves at 5 in the main flow of gas.

This almost ideal scheme has been quite successful, except that the close control over the quality of pitch which the inert gas recirculation procedure affords is not equaled.

The oil fraction is next divided into four fractions, which contain: (1) the light oil, benzene, toluene, xylene, some pyridine and naphthalene; it forms 10 per cent of the total, and boils up to 170° C. (338° F.); (2) the carbolic oil, phenol, naphthalene, and pyridine bases; it forms 10 per cent of the total, and boils up to 225° C. (437° F.); (3) the cresote oil, mainly cresols; it forms 10 per cent of the total, and boils up to 270° C. (518° F.); (4) the heavy oil, anthracene, phenanthrene, carbazol, forming 40 per cent of the

total, and boiling up to 320° C. (608° F.). The boiling points give those observed at atmospheric pressure; at reduced pressure, or with gas circulation, they are correspondingly reduced.

The refining of these fractions constitutes an important industry, because it furnishes the raw materials for dye manufacture, partly because its products are the basis for some of the military explosives which can be obtainable within the borders of the country for the emergency of national defense. The purification is mainly by distillation, caustic treatment, and sulfuric acid washing.

The processes are as follows ¹⁵:

(1) The light oil is distilled in fire-heated fractionating stills at reduced pressure; the shelves of the fractionating column have small holes and bells so that the rising vapors must bubble through the liquid. The products are crude benzene, crude toluene, crude solvent naphtha, and a residue of tarry nature which serves as fuel.

The various crude products are washed with sulfuric acid, then with caustic solution, and again distilled by themselves in steam-heated stills with columns, at atmospheric pressure. Pure benzene, toluene, and xylene are obtained; per ton of coal, the yield is 0.4 gallon toluene, 2 gallons benzene, and 0.2 gallon xylene.

(2) The carbolic oil is cooled in large shallow pans, where the naphthalene separates in the solid state; it is centrifuged to form crude naphthalene. The oil which remains is washed with caustic, removing the pyridine and phenol; then with dilute sulfuric acid, in order to dissolve the pyridine base.

TABLE 30.—United States production of certain coal-tar crudes (1940).
(U. S. Tariff Commission)

		Unit value
Tar	673,286,517 gallons	4.6 cents/gallon
Light oil and derivatives		
Crude light oil	216,617,985 gallons	8.0 cents/gallon
Benzene	36,555,643 gallons	12.9 cents/gallon
Motor benzene	101,140,079 gallons	8.4 cents/gallon
Toluol, crude and refined	30,440,324 gallons	24.7 cents/gallon
Solvent naphtha	9,230,139 gallons	17.9 cents/gallon
Xylene	5,645,993 gallons	23.2 cents/gallon
Naphthalene crude	159,637,499 pounds	2.0 cents/pound
Anthracene, cumene, cresylic acid.....	\$256,405 in value in 1935	
Pyridine	241,075 gallons	135.9 cents/gallon
Creosote oil	119,678,785 gallons	12.1 cents/gallon
Road tars	150,523,083 gallons	6.9 cents/gallon
Distillates including crude-tar acids, pyridine, phenol, sodium phenolate, and others	50,631,609 gallons	15.1 cents/gallon
Pitch of tar	707,082 tons	12.7 dollars/ton
Pitch of tar coke	90,906 tons	11.58 dollars/ton

the residue is distilled and gives essentially two parts, solvent naphtha distillate, and a resin (cumar) which is left in the still. The caustic solution is acidified to free the phenol, and the latter is distilled in fire-heated stills at reduced pressure; the product is a crude phenol, which must be redistilled in steam-heated stills. This distilled product is refined still further by mixing it with a little water, cooling it to a cake, crushing this,

¹⁵ Chem. Met. Eng., 23, 321 (1920).

lugging the mass, there is finally obtained the crystallized phenol of commerce.

The pyridine bases are recovered from their acid solution by adding lime, and then distilled.

The crude naphthalene obtained in the first step is purified by melting, cooling again, and centrifuging the semi-solid mass which results. The solid in the basket is melted again, distilled in fire-heated stills, and stillate agitated while melted first with sulfuric acid, then with caustic. The residue again distilled; the distilled material solidifies on cooling as the naphthalene of commerce.

Fraction (3) may be used as such.



FIGURE 95.—Ammonia still with continuous operation. At the right, the lime leg surmounted by column for free ammonia distillation; at left, the fixed leg. See diagram in Figure 80. (Courtesy of the Koppers Construction Co., Pittsburgh, Pa.)

4) The heavy oil solidifies on cooling; it is washed with solvent naphtha and filtered; the naphtha contains the phenanthrene. The filter cake is next washed with pyridine, to remove carbazol. The remaining solid is melted and condensed in large chambers, as a white solid; it contains 80 to 85 per cent anthracene.

The pyridine solution is distilled, yielding in the distillate first pyridine, then carbazol, a solid; the latter is washed with solvent naphtha and filtered; the product is 85 to 90 per cent carbazol.¹⁶

The formulas of many of these compounds will be found in Chapters 27 and 28.

Low-Temperature Carbonization. By carbonizing at a lower temperature than customary, a higher yield of liquid products, resembling oil than tar, may be obtained. The oven wall temperature in usual practice is 2350°F. (1288°C.); in the low-temperature processes, it would be 1300°F. (704°C.) and less. The difficulty is to perform the carbonization in a reasonable time; the temperature is so low that the rate of its penetration is also low. Very thin layers of coal have been tried; also carbonization by passing in hot producer gas. For the present, the low-temperature processes are not of industrial importance in the United States.¹⁷

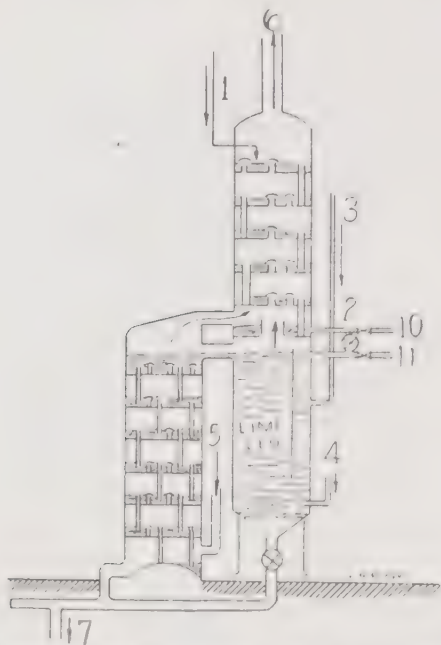


FIGURE 96.—Operation of ammonia still with continuous operation; Koppers system. 1, liquor inlet into the free still; 2, by-pass to the lime leg or mixing vessel, receiving lime at 3 and steam at 4; the milky suspension overflows to the fixed leg, receiving steam at 5; 6, ammonia vapors outlet; 7, waste pipe to sewer.

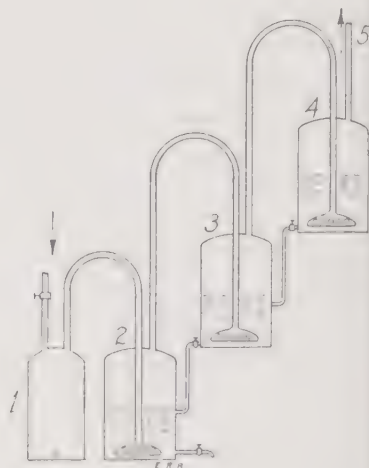


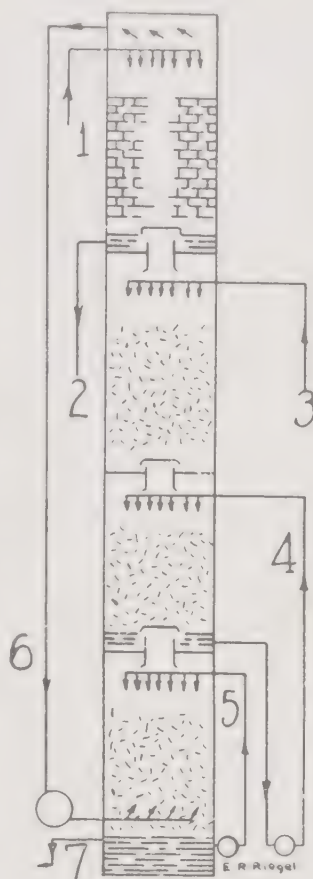
FIGURE 97.—Absorption of ammonia in water, using lead absorption bottles; the rich gas enters through trap 1, bubbles through 2, then 3, finally 4, and passes out, free from ammonia, at 5; the amount passing out is very small. The water from 4 is run into 3, and this into 2, where it is brought up to strength. Each bottle has a lead cooling coil, not shown.

Ammonia Distillation. The ammonia still shown in Figures 95 and 96 liberates ammonia gas in two distinct steps. The upper part of the tall vessel, to the right, is a six-plate tower, each plate with caps and run-off pipes. The liquor to be distilled is fed in at the top plate; the free ammonia is driven out by heat alone. By free ammonia is meant ammonium hydroxide, sulfide and carbonate. At the last plate, a liquor collects which has free ammonia, but still contains fixed ammonia, that is, sulfate or chloride, which must be treated with lime in order to liberate the ammonia. This liquor runs through by-pass 2 (see Fig. 96) to the lower part of

¹⁷ "Lessons from low temperature carbonization," R. P. Soule, *Proc. Intern. Coal. Bituminous Conf.*, Pittsburgh, Pa., 1, 272-298 (1931).

cool, where milk of lime is sent in. Liquor and lime mix thoroughly as they reach the overflow to the fixed leg, where they travel downward over plates with caps and through the run-down pipes to the pipe 7. A strong flow of steam enters near the base of the fixed leg, driving out the ammonia completely; the latter passes upward into the free end with the ammonia from that still passes through a dephlegmator to saturators, where ammonium sulfate is produced.

FIGURE 98.—Apparatus for dephenolizing ammonia liquors in coal distillation plants, by inert gas circulation (Koppers system). 1, phenol-bearing liquor; 2, phenol-free liquor; 3, fresh caustic solution; 4, circulated No. 2 caustic solution; 5, circulated No. 3 caustic solution; 6, inert gas laden with phenol vapors; 7, sodium phenolate solution outlet.



The same still may be used to produce ammonia aqua. For this purpose it is necessary to retain hydrogen sulfide and carbon dioxide; this is done by an additional caustic soda wash, in a short column with plates and bubble cap. The purified ammonia gas is absorbed in lead bottles. (See Fig. 97.) In regular coke-oven practice, the ammonia still receives only a small portion of the total ammonia in any form; the bulk of the ammonia in the coal gas goes directly to the saturators while still in the coke-oven gas, as stated under Ammonia Extraction. It is the increment in the ammonia liquor used in the spray which is sent to the still, together with the water layer in the condensate in secondary coolers. A certain amount of gas liquor will always have to be distilled because

small gas plants scrub their gas free from ammonia by water. The rising liquor is usually concentrated by a preliminary distillation, and sent to a chemical firm, where it is made into aqua or ammonium sulfate. In order to make sulfate, the still just described would be employed to free the ammonia gas, impure with hydrogen sulfide and carbonate, and the gas would be passed through a lead distributing pipe into a sulfuric acid solution partly saturated with ammonia. The salt formed may be shipped out by hand or may be removed by a steam ejector. The unabsorbed gas is piped under a fireplace, so that only sulfur dioxide and carbon dioxide need be discharged into the atmosphere.

The reactions with lime are: $2\text{NH}_4\text{Cl} + \text{Ca}(\text{OH})_2 = 2\text{NH}_3 + \text{CaCl}_2 + 2\text{H}_2\text{O}$; and $(\text{NH}_4)_2\text{SO}_4 + \text{Ca}(\text{OH})_2 = 2\text{NH}_3 + \text{CaSO}_4 + 2\text{H}_2\text{O}$. In the free still, they are: $(\text{NH}_4)_2\text{S} = 2\text{NH}_3 + \text{H}_2\text{S}$; $(\text{NH}_4)_2\text{CO}_3 = 2\text{NH}_3 + \text{H}_2\text{O}$, and several others in small proportion.

De-phenolizing Ammonia Waste. The chlorination of city water has at times led to a bad taste, traced to a phenol content in the water, originating in the waste from the by-product ammonia still in a city gas plant in any coke plant. The phenol is removed by taking the ammonia liquor at outlet 10 in the working sketch of the Koppers still (Fig. 96), and sending it through a de-phenolizing system such as shown in Fig. 98, wherein the phenol is removed in vapor form by an inert gas, which then is scrubbed with caustic. Sodium phenolate is formed, which is collected and removed to a storage tank; later the phenol is regenerated by treating with an acid. The phenol-free liquor returns by inlet 11 to the ammonia still, to receive the lime treatment.

Towers in which finely divided liquid benzene rises through ammonia water, dissolving any contained phenol, are also in use; unpacked towers are used, and the benzene travels counter-current to the ammonia liquor.

OTHER PATENTS

U. S. Patent 1,888,465, operation of by-product coke oven plant; 1,891,129, extractor for vertical (West) carbonization retorts; 1,841,036, enriched water gas from high-grade coke from caking bituminous coal; 1,838,294, coke oven battery (Becker); 1,805,922, horizontal coke oven (Otto); 1,829,608 and 1,787,490, vertical chamber coke oven; 1,787,963, coking retort oven; 1,832,181 and -2, coking retort oven; 1,831,451 and -3, coke oven (Becker); 1,893,145, on distilling tar residue by direct contact with hot gases at high temperature; 1,888,235-6, passing hot coke-oven gas through successive sprays of coal tar immediately after gas leaves the oven; 1,844,892, 1,868,394-5, 1,871,550, on using by-product recovery system of coke-ovens to recover clean tar oils; 1,871,596, continuous distillation by bringing tar into indirect counter-current heat exchange relation with hot coke-oven gases.

PROBLEMS

1. A by-product coke plant disposes of 3200 gallons of motor spirits per day, which is also the daily production. Using the yield figures in the text, how much water is distilled?

2. For the production of 315 tons of ammonium sulfate, how many tons of coke are coked, if the yield figures in the text apply?

3. In a Woodall-Duckham vertical retort, a coal is gasified which contains 19 per cent of combustible volatiles. Each ton of coal furnishes 13,350 cu. ft. of clean gas, ready for the holder. How much gas is due to the steam-on-coal reaction? (For water gas relations, see next chapter.) The gas from the coal occupies 20 cu. ft. per pound of weight.

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Fuel in the form of gas under slight pressure offers many advantages; its distribution costs little, once the pipes are laid; it is ashless, smoky, and its application requires very simple devices. The use of combu gas in municipalities is increasing, in spite of the newer electrical h devices. In the industries, gas is largely employed as a fuel.

Chapter 15

Combustible and Illuminating Gas, Water Gas, Producer Gas and Natural Gas

The typical combustible gases which are manufactured are coal gas, coke-oven gas, water gas, producer gas, and oil gas; natural gas is obtained from the earth.

Coal gas and coke-oven gas are very similar; both are made by the distillation of bituminous coal. By coal gas is meant the gas made in smaller retorts, either horizontal or vertical, in which coal is distilled primarily for the gas it yields; coke-oven gas is made in coke ovens, with coke gas both primary products. Coal gas is high in illuminants (benzene, ethylene); in former years, it was still higher, for the original horizontal retorts had a vapor space over the coal which was exposed to the same heat as the coal itself, and in this space nearly all the tar and oil "cracked," producing mainly illuminants. Since the introduction of vertical retorts, filled over the whole cross-section with coal, less cracking takes place, and coal gas resembles more closely the gas from coke ovens in which such cracking is also restricted.

Water gas is an entirely different product; it is made by passing steam through a bed of incandescent coke or other fuel; except for unimportant impurities it consists of hydrogen and carbon monoxide.

The manufacture of producer gas, on the other hand, is a continuous process; it is made by passing a mixture of steam and air into a bed of burning coke, anthracite, non-coking low-volatile coal, lignite, or peat. The resulting gas contains hydrogen and carbon monoxide as valuable constituents; nearly half of it is nitrogen, so that its heating value is low. Producer gas is used, after careful cleaning, in gas engines (internal combustion). Mond gas is producer gas made at low temperature so that the ammonia in the coal may be conserved and later recovered. Blast-furnace gas is also a form of producer gas.

Oil gas is made by "cracking"² suitable fractions of petroleum, in retorts poor in coal and lignite, but rich in oil; it is rich in illuminants and has a high heating value.

Natural gas is obtained from the soil, chiefly by means of deep wells; gas may issue from the well under pressure, or pumping may be required. It varies in composition, frequently containing a high percentage of methane, and just as frequently, non-combustible impurities; in general its heating value is very high.

¹ Chapter 47.

² Compare the cracking of oil for gasoline, Chapter 24.

There are many combinations of two or more of these typical combustible gases; the most frequent probably is that of oil gas and water gas, produced by enriching straight water gas by carburetted oil. In Buffalo at the present time the city gas consists of a mixture of coke-retort gas, coke-oven gas, water gas enriched by oil (hence containing oil gas) and natural gas.

The composition of several typical combustible gases is exhibited in Table 31; the constituents are listed in the order in which they are determined in the analysis; the figures are percentages by volume.

TABLE 31.—Composition of typical combustible gases.

	Straight coke-oven gas	Straight water gas	Water gas enriched by oil* Per cent	Producer gas	Natural ^{2a} gas
Carbon dioxide CO ₂	1.8	3.7	4.25	5.2	...
Benzene C ₆ H ₆9
Ethylene C ₂ H ₄	2.3	1.0	...
or other illuminants	10.33
Oxygen O ₂8	.5	.71	.2	...
Carbon monoxide CO	5.5	42.3	31.60	26.3	...
Hydrogen H ₂	49.2	47.9	35.38	14.4	...
Methane CH ₄	30.3	.6	12.40	1.8	90.0
Ethane C ₂ H ₆	8.8
Nitrogen N ₂	9.2	3.4	5.33	51.1	1.2
Total combustibles	88.2	90.8	89.71	43.5	98.8
B.t.u. per cu. foot	555	299	574	155.6	1110

* 3.10 gallons of fuel oil per 1000 cubic feet of gas for enrichment.

^{2a} As to natural gas, other kinds will be found occurring in the State; it should be remembered that some natural gases contain sulfur, some contain nitrogen in sizable amounts, others contain small quantities of unsaturated hydrocarbons. For the analysis of a wood gas, see Chapter 16.

An inspection of this table will show that the heat values of coke-oven gas and straight water gas differ markedly, yet their percentage of combustibles is about the same. The reason is that the component compounds have different heats of combustion; hydrogen evolves 329 B. t. u. per cubic foot, measured at 62° F. and 1 atmosphere; carbon monoxide 322, methane 803, ethane 1755. It is possible to compute the heat value of a mixed gas from the known values of the heats of combustion of the component gases; thus for the coke-oven gas listed in the table, the calculated heat value is 556 B. t. u.,³ while the observed value was 555. It may be noted also that producer gas has the lowest heat value; the same high temperatures which other gases furnish are nevertheless obtained with producer gas by heating it in regenerators; the need of heating a vast volume of inert ashes by the combustion itself is thus largely avoided.

The manufacture of coal gas and of coke-oven gas has been described in the preceding chapter.

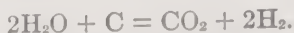
WATER GAS ⁴

Water gas is made by passing steam into a bed of incandescent coke; the temperature of such a fire is 1400° C. (2552° F.). Between the tempera-

³ A part of this gas is distributed to townships near Buffalo for direct consumption; it is there made slightly better than the New York State standard, 537 B.t.u.; there is no candle power and in New York State. Another part of this gas is mixed with natural gas and water gas, for distribution in the city of Buffalo; for this purpose it could be lower, since natural gas raises its value.

⁴ Also called blue gas, because it burns with a blue flame.

tures of 1400° and 1000° C. (1832° F.), the reaction $\text{H}_2\text{O} + \text{C} = \text{CO} + \text{H}_2$ takes place. As it proceeds, there is a fall in the temperature of the fire the incoming steam must be heated. The reaction itself is endothermic and heat is lost by radiation. With coke at a temperature below 1000° C. the steam reacts to form carbon dioxide, which is not desired, for carbon dioxide has no calorific value.



Hence the steam is stopped before the low temperature is reached, and the fire is brought back to its normal high temperature, 1400° C., by an air blast. Coke is consumed during the blast period, so that it could not be expected that all of it would be represented by carbon monoxide. Usually between 50 and 60 per cent is transformed into the lower oxide; the rest burns to carbon dioxide which escapes through a stack. There always are a few colder spots present, so that the second reaction takes place to some extent.

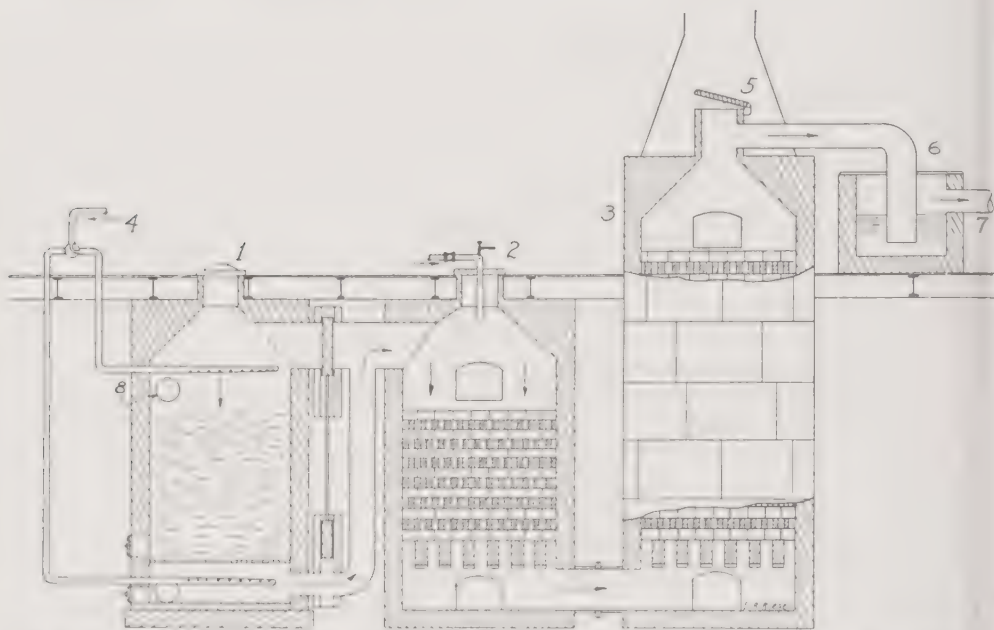


FIGURE 99.—Cross-section through a water-gas plant. 1. generator; 2. carburetor; 3. superheater; 4. steam inlet set for down-blow; the path of the gases is shown by arrows; valve 5 being closed, they pass through water box 6 to conduit 7 which leads to the purifying apparatus. 8 is the inlet for the blast during the revivifying period.

For many purposes, water gas is used as such; for sale in municipalities it is usually enriched with oil gas, produced in a separate vessel forming part of the system. The gas-making period lasts 4 minutes; the air-blast revivifying period, 2 minutes; the complete cycle is therefore 6 minutes. In order to use the hottest coke fully, the steam period is divided in two and the steam sent in from below for one half, from above during the other half. Simultaneously with the change of direction of the steam, one or two gas valves open, so that the gas formed is led off in either case through

wide flue to the off-gas vessel. After the steam has been on 3 minutes the apparatus is purged for 1 minute, and then only is the air blast turned on. The operations and their duration are then: $1\frac{1}{2}$ minutes for "up-blow," $1\frac{1}{2}$ minutes for "down-steam," 1 minute for purge, and 2 minutes for air blast.

The complete generating apparatus consists of 3 vessels; the generator, a carburetor, and the superheater. All are steel vessels, cylindrical, of somewhat differing heights and diameters, as indicated in Figure 99: the generator is 10 feet in diameter and 15 feet high. The coke fire is in the generator, the coke charge is shoveled in through an opening in its top, level with the working floor. The steam for the up-blow enters below the fire through a perforated circular distributor; the gas made passes out through the upper valve in the 42-inch flue to the carburetor. For the down-blow, the steam enters above, and the gas passes out through the lower valve which lies in the same vertical plane as the upper; a flue leads the gas to the upper horizontal flue, so that this gas enters the carburetor at the same place as the up-blow gas. The valves are slot valves, and being in one plane, are operated by one rod; the three-way steam cock connected with levers to this rod, so that a single motion (small compressed air cylinder) makes all the changes simultaneously. The generator and flues are brick-lined.

The carburetor is filled with a checkerwork of bricks; during the air blast, the products of combustion stream through and raise its heat. During the steam period, the made gas, at high heat itself, enters near the top and passes downward, while an atomizer delivers oil at the top of the carburetor. The current of gas carries the mist of oil against the hot checkerwork; the greater part is reduced to molecular fragments which at normal temperature form gases; at the same time, a certain amount of tar is produced. From the base of the carburetor the gases pass to the superheater, in which they stream upward, to be delivered to the flue leading to the purifying apparatus. The superheater is also filled with bricks, and provides space and heat to carry out the oil-cracking and the thorough mixing of the gases. The path of the gases is indicated in the general illustration.

The three minutes of steam blow are followed by one minute of purge, during which steam enters at the top of the carburetor and sweeps out the old gas which remains in the carburetor and in the superheater. At the end of four minutes, the blast is turned on, to bring the fire back to incandescence; the products of combustion, after passing through generator and superheater, escape through a stack just above the latter, through a valve in the flue leading to the purifying apparatus. Each time the valve opens, the waste gas catches fire with an explosion-like noise. Safety of operation is insured by interlocking devices, which permit the opening and closing of several valves only in the proper order.

For a generator of the dimensions given, coke of the egg size is introduced in 820-pound lots; the production is about at the rate of 1000 cubic feet of straight water gas to each 40 pounds of coke consumed (total). To each cubic foot of gas, varying amounts of fuel oil or special gas-oil fraction are

used, for instance $3\frac{1}{2}$ gallons per 1000 cubic feet of water gas; in the case described, this would require 20 gallons per cycle. The temperature in the carburetor lies between 1200 and 1300° F. (650° and 704° C.), and is measured by means of pyrometers.⁵

In an oil-gas plant, a generator and superheater are used, and the heat is furnished by an oil burner; otherwise the operation is similar to the one just described.

The Purification of Carburetted Water Gas. The flue leading away from the superheater dips in the water of the wash-box, where the small amount of tar is deposited; the gas then passes to the cooler, a nest of pipe laid in running water. From here it is pulled by exhausters and pushed into the purifying boxes containing the same lime-iron oxide-coated shavings which are used for coke-oven gas.⁶ From the purifying boxes, the gas passes to the holders, ready for delivery. Metering and testing are performed by the continuous, recording Thomas meter and Thomas calorimeter already described (Chapter 14).

A water-gas plant is compact; it may be started at short notice, and when shut down for a given period is readily maintained in good condition. When part of a system supplying municipalities, it is usually shut down in the summer months, when the demand is light enough to be supplied by coke-oven gas or coal gas; it is placed in operation in the winter months.

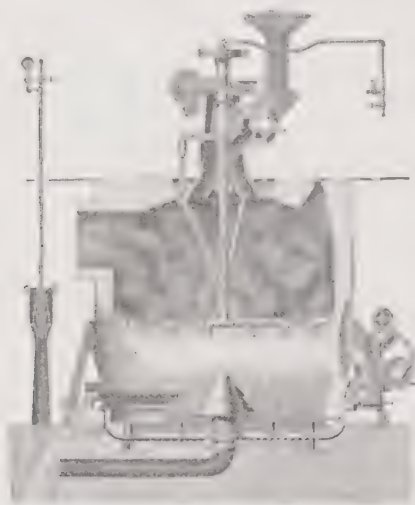


FIGURE 100.—The Chapman Gas Producer with stationary shell. (Courtesy of the Cooper-Bessemer Corporation, Mt. Vernon, Ohio.)

PRODUCER GAS

The modern producer is a steel vessel of moderate size; as for example 6 feet in diameter and 12 feet in height, brick-lined; in it any low-grade fuel may be partly burned, while steam in addition to air is sent into the fire. The operation is continuous; the fuel (for instance, low-grade coal) is dropped into the producer at a constant rate. A mixture of air and steam is served all the time. The made gas passes out continuously, and the ashes are removed constantly by a sweeper in the water seal at the base.

⁵ Chapter 46.

⁶ For "liquid purification" see previous chapter.

such a producer is shown in Fig. 100; it carries a water-cooled, rotating arm which levels the charge and prevents the formation of holes. The shell is stationary. The reactions are essentially the same as those which take place in a water-gas plant; but in producer gas there is contained all the oxygen entering with the air for combustion; hence its total combustible constituents are low, and its heat value per unit volume also. Numerous types of producers are on the market; in some of these, the shell rotates.

The capacity of a producer 10 feet in diameter and 12 feet high with automatic operation, is 3000 to 4000 pounds of coal per hour. The air-gas mixture is forced in by means of the steam which is applied to an air heater (see illustration); the composition of this mixture is approximately 7 volumes air and 1 of steam. The amount of steam used per pound of coal gasified lies between 0.3 and 0.5 pound, sometimes a little lower, 0.25; the amount depends upon the clinkering properties of the coal used. The volume of gas varies with the grade of coal. The following figures will serve as guides: 1 pound of bituminous coal yields 60 cubic feet; sub-bituminous, 30 cubic feet, and lignite, 28 cubic feet.

NATURAL GAS

Natural gas is found in regions which also have coal or oil, although the wells may be many miles away. Many gas wells do not yield oil, but an oil well almost always produces gas and oil, the gas is then known as singhead gas. The gas from wells which yield no oil is usually rich in methane and contains some ethane and higher hydrocarbons; its composition remains fairly steady over long periods. The gas obtained with oil (petroleum) is at first methane essentially, but gradually becomes richer in the higher hydrocarbons, and poorer in methane; such gas when "wet" furnishes a very volatile gasoline, casinghead gasoline, which is largely used in mix with "cracked gasoline" deficient in low-boiling constituents. The methods for extracting gasoline from such gas are compression and cooling, and absorption by a higher-boiling oil fraction, by charcoal, silica gel, or other absorbent. Gasoline extracted from natural gas in 1940 made a new record, 2,320,458,000 gallons which brought the low price of 1 cent per gallon. The production of gasoline from wet natural gas, in the leading states, expressed in millions of gallons, was as follows: Texas 920, California 586, Oklahoma 399, Louisiana 109, Kansas 64, West Virginia 56.8, and New Mexico 55.

The residual gas after gasoline removal is used as fuel, as is gas from wells yielding no gasoline; but appreciable amounts are burned with an insufficient amount of air for the production of carbon black, or decomposed with heat to form carbon and hydrogen. The development of the natural gas trunk pipe lines has brought about a distribution of this gas which makes it rival of manufactured gas; as stated before, it is often admixed with coke-oven gas for domestic use. There is a gas trunk line from Amarillo, Texas, to Chicago; another to Indianapolis; in the South and Southeast, a line runs

The gas for the chemical laboratory of the University of Buffalo, within the city limits, is taken from a well just outside the boundary; it is one foot deeper, the pressure in the well is 260 pounds per square foot. The well has furnished gas under the same pressure for many years past. The amount drawn is moderate.

from Shreveport, Louisiana, to Atlanta, Georgia. There are many shorter lines; in 1940 the gas pipe lines totaled over 70,000 miles. No gas pipe lines cross the Rocky Mountains.

The marketed production of natural gas for 1940 (U. S.) was 2,67 billions cubic feet, a new high record; the gross production would be about a third more. Roughly, half the gas is from oil wells, half from gas wells. Of the natural gas consumed, 89 per cent was treated for the removal of gasoline values. The production for the leading states, expressed in billions of cubic feet, was as follows: Texas 1,090, California 360, Louisiana 320, Oklahoma 265, West Virginia 180, Pennsylvania 86.



FIGURE 100a.—Three insulated nickel steel spheres containing liquefied natural gas. The temperature of the gas is approximately -250°F . The vapor pressure in the spheres is about 5 pounds psi. (Courtesy of The East Ohio Gas Company, Cleveland, Ohio.)

The average value of natural gas at the well and unprocessed was 10 cents per 1,000 cubic feet in 1940; the residual gas after washing out of gasoline values brought $1\frac{1}{2}$ to 2 cents per 1,000 cubic feet. The total number of producing gas wells in 1939 was 53,530, and to these were added 2,382 wells drilled in 1940.

Not only in gas form, but also in the liquefied state is there a large movement of low molecular weight hydrocarbons, of petroleum as well as of natural gas origin. In 1940 there were marketed 109.2 million gallons of liquefied propane, 77 million gallons of butane, 123 million gallons of propane-butane mixture, and 3.8 million gallons pentane. These liquefied hydrocarbons are shipped in tank cars and tank wagons, in cylinders, drums, and by pipe line. The industrial uses account for 22.3 per cent

the total, the domestic (household) uses for 43 per cent, the gas manufacturing industries for 6.5 per cent. Some of the industrial uses are given in Chapter 24. (All figures in this section from Minerals Yearbook, 1940).

Supplementing the natural gas flowing in gas form along the feeding line, there has been placed in operation a set of double walled, spherical storage tanks (3) containing liquefied natural gas, to be drawn on for peak load supply, in Cleveland.^{7a} The inner spherical tank is 57 feet in diameter, and made of low carbon (0.09%) nickel (3½%) steel; the outer tank is 63 feet. The space between the two is filled with granulated cork. The temperature within the container is low, -250°F. (-157°C.) the pressure is low. The capacity of each tank is 60,000 gallons, equivalent to 50 million cubic feet of free gas. The complete plant includes compressors, ethylene and ammonia refrigerants, and evaporation equipment.

Pintsch gas is a compressed oil gas. Blau gas is a mixture of propane, butane, pentane, and hexane containing hydrogen and methane in solution under pressure. The solution is handled in strong steel cylinders. Acetylene is presented in Chapter 19. For isolated laboratories a satisfactory burning gas is obtainable by bubbling air through a low-boiling gasoline; the regulation is automatic, a reduction in pressure of the gas causing a water valve to open, whose flow rotates a water turbine which carries the fan. Another convenient gas for isolated laboratories is "Pyrofax," which is propane, C_2H_6 (boiling point -42.5°C.) compressed in steel cylinders which are transportable. Similar "bottled gases" are Philco, Essotane, and many others.

SURFACE COMBUSTION

Surface combustion is flameless combustion; it takes place when gas strikes the theoretical amount of air strikes lumps of refractory materials which are at high heat; this material glows, and high temperatures are attained. Instead of lumps, a slab or a brick wall may be used. The advantages of this method of combustion are that the combustion is moderated, that the energy appears largely as radiant energy which is easily transmitted, and that the source of this energy is concentrated. Places have been heated by this method, but of special interest is the construction of a boiler⁸ with fire tubes which were filled with refractory materials on which the combustion took place. The boiler was 4 feet in diameter, and without brick setting; the generation of heat took place within the 4-foot fire tubes. This unusual method of heating affords important economies.

Surface combustion is a catalytic process; the combination of gas and oxygen is accelerated by the contact substance, here fragments of firebricks. It may be applied with water gas, coke-oven gas, natural gas; whether water gas may be used is not quite settled.

^{7a} "Drawing natural gas for peak load supply," by R. W. Miller and J. A. Clark, *Chem. Met. Eng. Progress*, p. 74 (1941).

⁸ "The use of its scientific uses," William A. Bone, who developed this boiler. London and New York: Mans, Green and Co., p. 445, 1918, or *Proc. Am. Gas Institute*, 6, 565 (1911).

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PROBLEMS

1. The composition of the several commercial combustible gases in the text are given in volume percentages. The heat of combustion for the several constituents in pure form is as follows: Ethylene, 1591 B.t.u. per cubic foot; carbon monoxide, 322; hydrogen, 329; methane, 1003; ethane, 1755; benzene, 4004 (for low percentages only) disregard the non-combustible gases. Compute on the basis of the percentage composition and the heat value for the substance, the heat value or heat of combustion for the several mixed gases given in the table; compare with the B.t.u. value reported there. There should be close agreement. These figures are all in terms of the "high B.t.u." results. (Figures from Marks' "Engineering Handbook," New York, McGraw-Hill Book Co.)

2. Find the corresponding volumes of typical combustible gases which must be burned to fit Problem 1, Chapter 12, in cubic feet at 62° F. and atmospheric pressure.

3. It is necessary to furnish 50,000 cu. ft. of producer gas per hour to a furnace. Using the yield figures given in the text, how many pounds of bituminous coal, semi-bituminous, and lignite will be required per day?

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"First commercial liquefaction plant in full-scale operation," P. A. Condit and W. T. Burgess, *The Oil and Gas Journal*, 39, part 5, March 20, p. 46 (1941).

The store of coal in the earth was formed many thousands of years when it is exhausted, man will not be able to replace it. It is different with wood, which can be grown within a few years; the scientific exploitation of the forest resources provides for replanting so that new wood grows about the same rate as older wood is cut. To put the difference in other way, using coal means the exhaustion of capital; using wood means drawing on earnings only.

Chapter 16

The Distillation of Hardwood for Charcoal and By-Products; the Hydrolysis of Wood

Distillation of hardwood for charcoal, with the recovery of the volatile products, pyroligneous acid and wood-tar, has taken the place of the process of making charcoal by the slow burning of a pile of wood covered with earth. By-product retorts bear the same relation to charcoal kilns as by-product coke ovens bear to beehive coke ovens. On refining pyroligneous acid there are obtained methyl alcohol (methanol), CH_3OH , acetone, $\text{CH}_3\text{CO}\cdot\text{CH}_3$, acetic acid, $\text{CH}_3\cdot\text{COOH}$, and a number of less important substances. The tar yields guaiacol, $\text{CH}_3\text{O}\cdot\text{C}_6\text{H}_4\cdot\text{OH}$ (1,2), creosol, and pitch. From the acetic acid, acetic anhydride or acetone may be made. The products are all of importance in chemical technology. Methanol is a good solvent for shellac, other gums, and resins; it is a preservative, and the raw material for the manufacture of formaldehyde. Acetic acid and acetic anhydride play a major rôle in the manufacture of nitrate silk.

Until a few years ago, this industry seemed securely established; since then, three newer developments have threatened it. Acetone is made by fermentation process, and by a synthetic process. Methanol is produced in large quantities by synthetic means. Acetic acid is manufactured from ethylene. All these processes are described in detail elsewhere in the book. It seems likely that the hardwood distillation industry will continue nevertheless, thanks to domestic and industrial demands for charcoal, and to improvements in the recovery of the by-products.

The industry is of importance in the states of Pennsylvania, New York, Michigan, and Tennessee; charcoal is made in Sweden and Norway, mainly without by-product recovery. Canada has hardwood distilling plants in the provinces of Ontario and Quebec.

Retort with Steel Buggies. In the older practice, 2 cords of air-dried wood (beech, maple, oak, hickory) cut in 4-foot lengths, are piled on a steel buggy; four buggies are pushed into a retort, 55 feet long, which they fill. The retort is made of steel, with an outer brick shape which leaves a space around the sides and top in which the fire gases circulate. The doors are closed, and heat applied by burning natural gas or oil. Two openings in the rear wall allow the volatile products to pass out.

The cycle is 24 hours: during the first few hours, the heating is rapid, in order to reach the distillation temperature; water comes over first. An

exothermic reaction takes place next, when the outside heat must be decreased: the valuable vapors begin to pass out. After about 10 hours the flames in the burners are raised again, but not as high as at first. At 22 hours, the distillation is over; all burners are turned off, and the retort is allowed to cool for 2 hours.

The buggies are placed in air-tight cooling chambers for two days, with a quenching spray of water after the first day. The charge shrinks considerably during the distillation, but the charcoal is obtained in the form of rather large pieces, and very little dust.

A cord of seasoned wood weighs about 3000 lbs.; the charcoal produced is about 1000 lbs., and the amount of permanent gas 7000 to 9000 cubic feet.



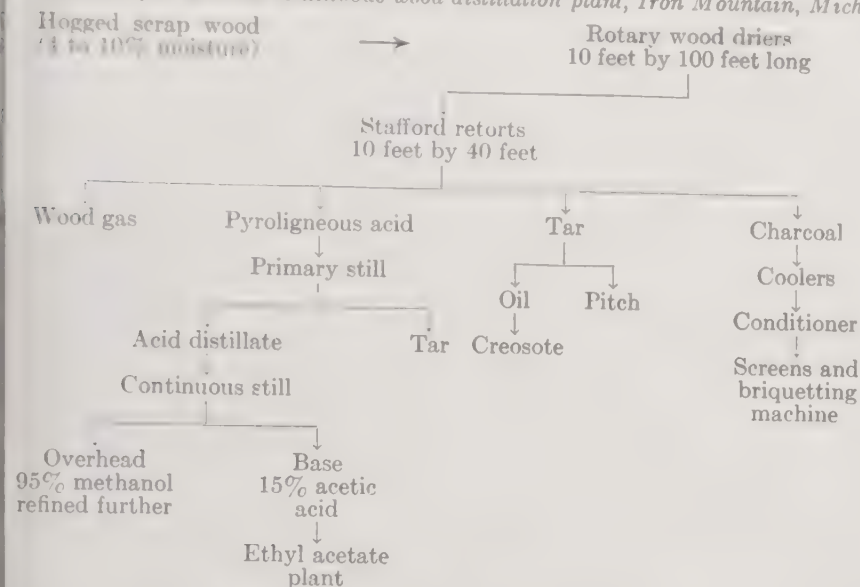
FIGURE 101.—Operating floor of the retort department. The top of the Staff retorts (3) are flush with the floor; around each retort, four condensers are grouped. Each retort has a feed pipe terminating in a motor-driven barrel valve. The pipe with the offset leading out of each retort is for the fire-gases during preheating period. (Courtesy of the Ford Motor Company, Dearborn, Mich.)

Retorts with Continuous Operation. The wood-distillation plant of the Ford Motor Company is a departure from the old practice not only in the acetic recovery method, but also in the retorts for distillation. They operate continuously; and still another difference is that the heat comes entirely from the exothermic reaction with which all wood distillers are familiar; a newly cleaned retort must be brought to the proper temperature by burning wood gas, but once the necessary temperature, 540°C . (1000°F .), has been reached, no external heat is needed.

¹ A table will be found on p. 10 of "Distillation of hardwoods in Canada," by Bates; see reading references.

The plant was erected in order to utilize the scrap wood from the automobile body plant; it was desired not to make acetic acid, but ethyl acetate, which the Ford Company requires in its lacquer and artificial leather departments. (See Fig. 101.)

Flow sheet for the Ford continuous wood distillation plant, Iron Mountain, Mich.



The operation may be described as follows:² The scrap wood is reduced to small size (up to 8 inches by 2 inches by $\frac{3}{4}$ inch) in a hog mill, passed through a drier reducing moisture to 0.5%, and fed through barrel valves³ to the top of the Badger-Stafford retorts. These are vertical cylinders of 10 feet wide by 40 feet high, with a heat-insulating inside wall 18 inches thick, composed of fire-brick, diatomaceous earth, and insulating brick. The heat developed by the exothermic reaction near the center of the retort rises with the vapors and gases developed, and warms the incoming charge until it reaches the reaction temperature and itself distills. The average temperature in the center of the retort is 515° C. (950° F.) near the bottom, 255° C. (490° F.). The carbonized material is discharged at the bottom through a barrel valve (Fig. 102). The charcoal passes into a cooler 6 feet in diameter and 30 feet long, cooled by water spray and a trickle of water on the outside. It passes next to the rotary conditioner, where it absorbs oxygen; the heat of absorption is dissipated by spraying water over the outer walls. It is now ready for screening and briquetting. The conditioning takes 5 hours, instead of 48 hours in the standard buggy coolers.

The gases and vapors passing out of the retort are cooled, the condensed pyroligneous acid is stored, the gas is scrubbed and blown to the power

From a description kindly furnished by the Ford Motor Company.

A barrel valve may be said to consist of two barrels, one fitting inside the other, and the inner barrel rotated by turning its axis; the inner barrel has two staves missing, so that the charge falls out of it. By turning, the charge is dumped, while the vessel at the same time is sealed.

house and burned under boilers, except the part which is used to bring fresh retort to the proper temperature.

After operating two weeks, a retort must be taken off the line, the accumulated tar burned out; it is then brought up to temperature burning wood gas in it for 24 hours.



FIGURE 102. First floor of retort department, showing the bottom and charcoal discharge end of the Stafford retort. The bars for shaking the grates are visible in upper center. The motor-driven barrel valve conveys the charcoal to the cooler, which extends beyond the wall to the left. The head of the second cooler is visible. (Courtesy of the Ford Motor Company, Dearborn, Mich.)

The pyroligneous acid is settled and distilled from batch primary still to remove dissolved tar. The acid distillate then goes to a continuous still which gives overhead 9.5 per cent methanol, and at the base 15 per cent acetic acid.

The methanol is refined in two discontinuous stills, whose seven "cuts" are refined further to give 75 per cent methyl acetone, 75 per cent methyl acetate, and C. P. methanol.

The 15 per cent acetic acid is treated with ethyl alcohol in the presence of sulfuric acid, to give a crude ethyl acetate; this is treated with calcium chloride, giving finally dry, pure ethyl acetate. The average yield of the various products is given in Table 32.

The wood used is 70 per cent maple, 25 per cent birch, and 5 per cent ash, elm and oak. The plant is designed for a capacity per day of 4 tons of scrap wood.

The average composition of the gas from the Badger-Stafford retort is hydrogen 2.2 per cent by volume, dry gas; methane 16.8; C_nH_m 1

TABLE 32.—Average yield of various products at the Iron Mountain Plant, Ford Motor Company, per ton of dry wood, 1936.

Charcoal	649 pounds
Gas	5000 cubic feet
C. P. methanol	3.66 gallons
Methyl acetate (and methyl acetate)	1.46 gallons
Allyl alcohol	.05 gallon
Ketones	.30 gallon
Methyl acetate	0.945 gallon
Soluble tar	37.46 gallons
Pitch	66.0 pounds
Creosote oil	3.25 gallons
Ethyl acetate	14.65 gallons
Ethyl formate	1.27 gallons

Carbon monoxide 23.4; carbon dioxide 37.9; oxygen 2.4; nitrogen 16.0; heat value, B. t. u. per cubic foot 290.

DIRECT RECOVERY OF ACETIC ACID

In the early days, the plant in the mountains made its acetic acid transportable by changing it into calcium acetate, which involved neutralization with lime, and evaporating to dryness. The customer had to distill this acetate with sulfuric acid in order to obtain the free acid. The develop-

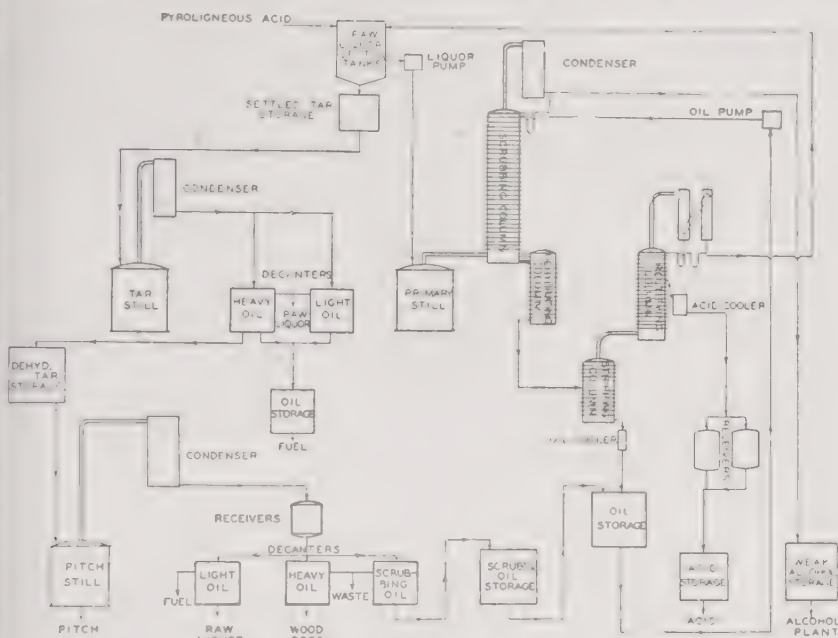


FIGURE 103.—Flow sheet of the Suida process for the extraction of acetic acid directly from the pyroligneous acid vapors. (Courtesy of Forest Products Chemical Company, Memphis, Tenn.)

ment of synthetic acetic acid made it economically impossible to continue this procedure; the wood distillation plants were the more pressed to reduce costs, in that synthetic methanol had cut the price of their second product, and alcohol. Three processes have been invented and perfected by the

users, in which the acetic acid is extracted from the acid distillate means of solvents, with subsequent separation by distillation. The Brews process uses isopropyl ether as the solvent; the Suida process uses a high-boiling wood-oil fraction, produced from the wood in the plant, and used over and over again for a reasonable number of cycles. The expense of buying a dissolving agent thus disappears in the Suida process, and acetic acid of 92 per cent strength is produced of high purity. Another process is the Othmer process. When it is added that in some states there is a steady market for charcoal for domestic use, it will be seen that, unhappily, this interesting industry has a new lease on life. The Brews process, it might be added, is particularly applicable to the recovery of acetic acid in a cellulose acetate plant.

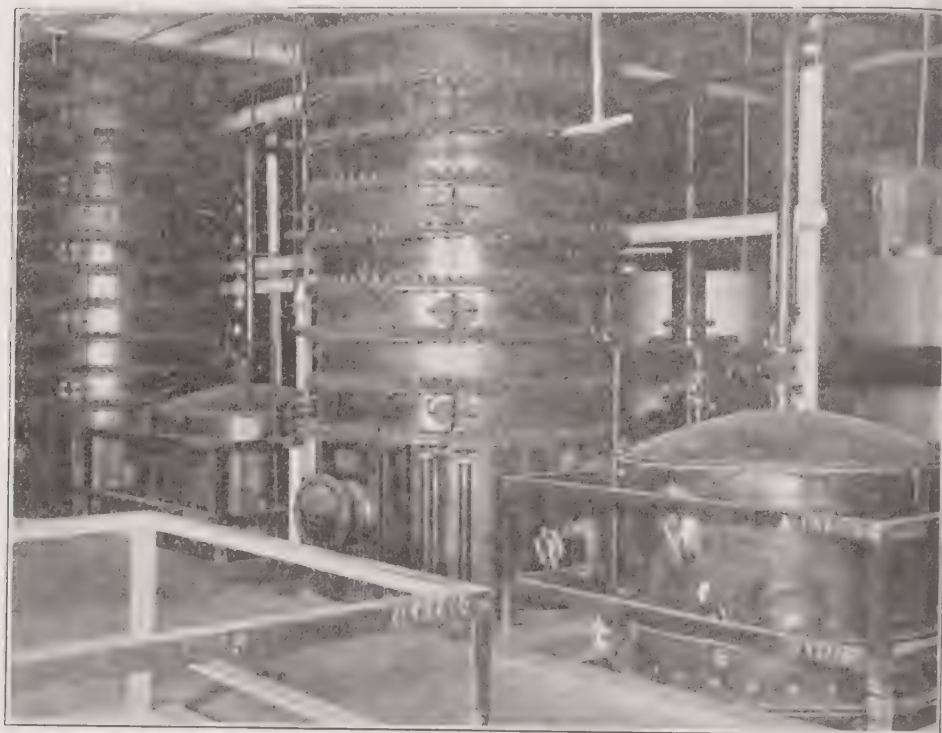


FIGURE 104.—The Suida process. Scrubbing columns, with the tops of the dehydrating columns shown. (Courtesy of Mr. T. C. Albin, Forest Products Chemical Co., Memphis, Tenn.)

The Suida Process.⁴ The apparatus, aside from retorts and the cooling and condensing equipment, includes a primary boiler, a scrubbing column, a dehydrating column, the second boiler, a stripping column (10 plates), a rectifying column (30 plates), a still for tar, and one for pitch, both with condensers and receivers. (See Fig. 103.)

The extraction is carried out in the superheated vapor phase. The settled pyroligneous acid is run to the primary still, which sends out vapors of acetic acid, alcohol, and water, retaining the dissolved tar, which

⁴ "Acetic acid and cellulose acetate in the United States," E. P. Partridge, *Ind. Eng. Chem.*, 482 (1931); "Suida process for acetic acid recovery," E. P. Poste, *Ind. Eng. Chem.*, 24, 722 (1932).

off periodically. The heating is by closed steam coils, and the vessel coils are of copper.

The vapors of acetic acid, crude methanol, and water enter at the base of the column, called the scrubbing column. (See Fig. 104.) Solvent oil enters near the top of the column and flows downward, while the vapors rise upward. The solvent oil takes up acetic acid vapors and some water. Crude oil charged with acetic acid and some water is drawn from the top of the tower; crude methyl alcohol, aldehydes, and water pass out of the column at the top. This overhead distillate is condensed and, for the most part, run to the weak alcohol storage; a small amount is returned to the still as reflux. The oil with acetic acid passes down the dehydrating column, and from there to the second boiler (not shown on flow sheet), which transfers the heated liquid to the stripping tower, operated under vacuum. The acetic acid vapors are flashed off (that is, vaporized with explosive effect) and enter the rectifying column, carrying a small amount of oil with them and all the water present. The lower part of the stripping column serves to exhaust the oil of acetic acid. In the rectifying column, oil is retained on the first few plates, and acetic acid of 92 per cent CH_3COOH is drawn off from the twelfth plate from the bottom. The upper plates receive most of the water which entered the rectifying tower; they have an acetic acid solution which becomes gradually weaker. There passes out at the top a 15 per cent acetic acid which is condensed and returned, directly to the pyroligneous storage.

The solvent oil leaves the stripping tower free from acid; it is cooled and returned to the scrubbing tower. It is obtained in the first place as follows: the tar is distilled and the distillate gives a light oil, and a heavy fraction. The latter is placed in the tar still, and distilled again. The distillate is divided into light oil, heavy oil, and scrubbing oil; it is the scrubbing oil fraction which serves as solvent. The excess is sold or burned as fuel. In the *Othmer process* ^{4a} for direct acetic acid, a "withdrawing agent" such as ethylene chloride or butyl alcohol, is added; there distills over an azeotropic mixture, with water one of its components. On cooling the mixture, the "withdrawing agent" forms a separate layer so that it is readily separated and used over again. The acetic acid, free from water, is left at the bottom of the still.

Several additional observations are in order. As modified in the American practice, the methanol need not be removed in a preliminary distillation from the pyroligneous acid; distilling the alcohol simultaneously with the acid, the use of acetic acid by the solvent reduces by half the amount of esters formed; to that extent the alcohol as such is preserved, and also the acid. The fact that which finds the production of calcium acetate no longer profitable has caused the change into a Suida plant, using the same retorts. Pure acetone formerly was made exclusively by the distillation of calcium acetate; it is now obtained by fermentation or by synthesis.

As to future trends, "both the wood distiller and the producer of synthetic acetone from acetylene are open to the danger of competition from newer

U. S. Patents 1,804,745 and 1,917,391. See further: "Dehydrating aqueous solutions of acetic acid," *F. Othmer, Chem. Met. Eng.*, 40, 631 (1933); and 41, 81 (1934).

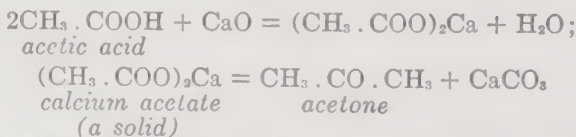
and cheaper synthetic processes. One of the possibilities is the oxidation of ethanol to acetic acid. The ethanol may be derived from fermentation or be made by synthesis from ethylene."⁵ This latter development would be due in great part to the loss of the regular market for ethanol, displaced by the cheaper synthetic methanol.

There were produced in 1939, 24,910,005 bushels of charcoal (12.5c), 4,883,978 gallons of crude methanol (wood alcohol) (17.7c), 11,279 tons of acetate of lime (\$27.50), directly recovered acetic acid 53,855,475 pounds (4.7c), and 8,898,977 gallons of tar (15c).

Refining the Alcohol. The crude alcohol fraction is separated into a number of purer substances in a continuous distillation with plate towers similar to the procedure used for ethyl alcohol, fully described in Chapter 20. In a crude containing 82 per cent organic substances, there are 6 to 10 per cent methyl acetate, $\text{CH}_3 \cdot \text{COOCH}_3$, 12 to 14 per cent acetone, 65 per cent methanol, and not over 1 per cent other organic bodies such as allyl alcohol, $\text{CH}_2 = \text{CH} \cdot \text{CH}_2\text{OH}$, and methyl ethyl ketone $\text{CH}_3 \cdot \text{CO} \cdot \text{C}_2\text{H}_5$. The separation is mainly in four grades: acetaldehyde, boiling at 20°C . (68°F .); acetone with 28 per cent methyl acetate, 51 per cent acetone, and 21 per cent hydrous methanol, used as an excellent solvent for nitrocellulose under the name of "methyl acetone"⁶; a high test methanol, and the allyl compounds.

Acetaldehyde may be transformed into paraldehyde, a polymer $(\text{CH}_3\text{CHO})_3$, by the action of a small amount of concentrated sulfuric acid. Paraldehyde is a liquid boiling at 128°C . (262°F .); it is a valuable hypnotic.

Acetone from Calcium Acetate. Acetone is made by fermentation of starch, with butyl alcohol as a second product (Chapter 20), but the older method might be mentioned, for, in an emergency, it could be revived. Dilute acetic acid is treated with lime, to form a solution of calcium acetate, which is concentrated to dryness; the solid is then heated, when it breaks down to form acetone and calcium carbonate. After the heat is removed, steam is blown into the vessel in order to drive out all the acetone. The boiling point of acetone is 56°C . (133°F .).

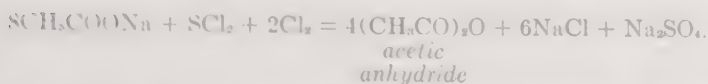


Acetic Anhydride. A portion of the acetic acid production is used to make sodium acetate, and this in turn serves as raw material for the manufacture of acetic anhydride. The method consists of mixing sodium acetate with sulfur chloride (SCl_2) and passing in chlorine, maintaining a temperature of 15° to 20°C . by cooling coils⁷; after the reaction is complete, the reaction mixture is heated two hours to 80°C ., and then the acetic anhydride is distilled. The latter boils at 138°C . (glacial acetic acid boils at 119°C .), and is best distilled at reduced pressure. The reaction is:

⁵ *Ind. Eng. Chem.*, E. P. Partridge, 23, 488 (1931).

⁶ Acetone is not isolated as such from crude wood spirits; methyl acetate and acetone form a constant boiling mixture.

⁷ German Patent 273,101, an improvement on 222,236, 241,898, and 132,605



In other patent proposals, successfully demonstrated, the sulfur chloride and sodium acetate are mixed with acetic anhydride, and then chlorine is passed in.

Acetic anhydride has a penetrating, painful odor. It is used in the manufacture of cellulose acetate, in the dye industry, and in the preparation of many pharmaceuticals.

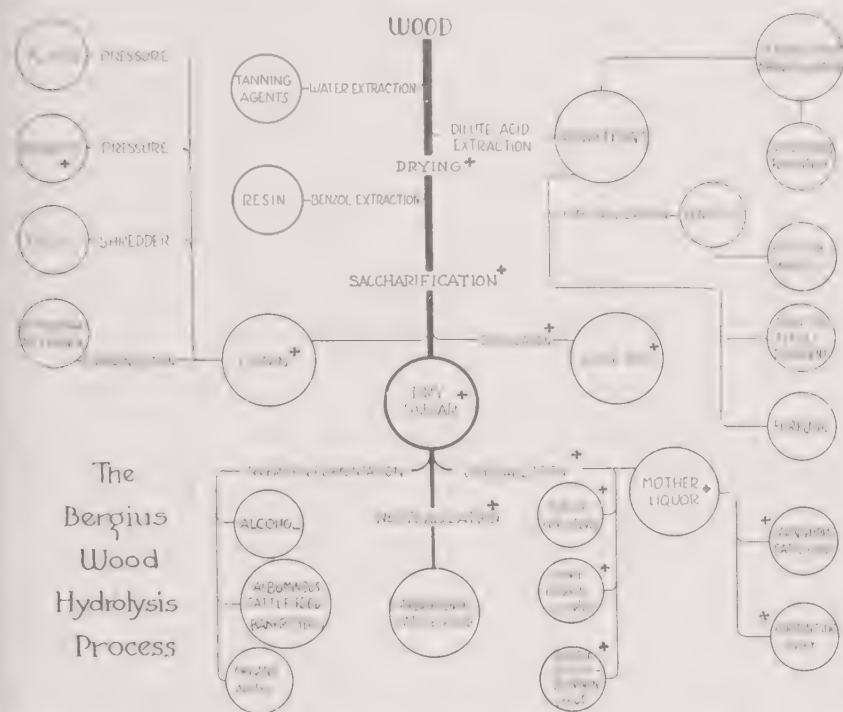


FIGURE 105. The complete products diagram for the Bergius wood hydrolysis process, not fully realized in the present practice (1936). The steps and products actually on a factory scale are designated with an asterisk (by ERR). The inversion-fermentation is an alternate to the sugar production. The water, dilute acid, and benzene extracts must precede saccharification. Based on the original German sketch kindly supplied by Dr. Friedrich Bergius.

BERGIUS PROCESS FOR WOOD HYDROLYSIS

The conversion of wood cellulose to sugars suitable for animal and human consumption by hydrolyzing it with hydrochloric acid in the cold on the commercial scale is an accomplished fact. The world is indebted for this contribution to the genius and persistence of Dr. Friedrich Bergius. On treating the chipped wood⁶ with 40 per cent hydrochloric acid at 100°C [168°F] in a bank of extractors or diffusers, there is produced a liquid, the hydrolysate, and a brown solid residue, the lignin. The hydrolysate is distilled in order to remove and recover the hydrochloric acid, and

⁶The wood studied has been pine, in one extended run, and beech, in another.

the acetic acid which pass out at the same stage; the two are separated. The concentrated residue is dried and is then the raw sugar, with some residual acid. The lignin retains the skeleton form of the wood chip; in the present it is made into briquets, but better uses, such as various types of molded products, are in process of development.

The raw sugar after a lime treatment is an acceptable cattle food. The tetrameric sugar molecules may be inverted to give the glucose, and may be the basis of a glucose syrup, or after further purification and decolorization will produce crystal glucose. If preferred, the sugars may be fermented to give ethyl alcohol; in this case, about 80 per cent of the sugar (glucose-ferments, but the residue, xylose and galactose, are best worked up in cattle feed).

An annual production of 6,000 metric tons of raw sugar was expected for 1936.

A number of further details will be gleaned from the accompanying flow sheet and product diagram. Numerous questions as to the choice of material for construction had to be solved.⁹

It should be noted that this process recovers as sugars the same matter which in the ordinary wood distillation goes out as carbon dioxide and water. The same values in acetic acid, alcohol, and lignin are obtainable besides, and in spite of the hydrolysis. Also, waste wood, not otherwise utilized at all, may be the raw material.

TURPENTINE AND ROSIN

Pure gum turpentine is obtained by steam-distilling the sap of the Southern pine, *Pinus Pinaster*; it consists principally of terpene hydrocarbons of the general empirical formula $C_{10}H_{16}$. Wood turpentine is produced from stumps and top wood by destructive distillation, ["DD"], or steam distillation ["SD"], by extraction with solvents ["SD"], or as by-product of the sulfate paper mills. The States most prominent in these industries are Florida, Georgia, Alabama, and Louisiana. The Scandinavian peninsula produces turpentine from the Norway pine; another producing area is along the coast in South-western France.

For the gum turpentine, incisions are made in the trunk of the pine leading into a cup which can hold one-half to 1 gallon of sap; the sap flows from March to September. The collected sap is distilled from a copper still; turpentine and water pass over, and the rosin is left in the still. In some plants, steam is passed in from the beginning; in others it is introduced after the turpentine and water distillate stops, giving an additional amount. The average composition of crude gum is rosin 68 per cent; turpentine 20 per cent; water 12 per cent. Its uses are based mainly on its solvent properties in paints; its high content of pinene permits the manufacture of pinene hydrochloride, a solid, and other chemical substances.

For the crop year April 1940-March 1941, there were produced: gum turpentine 343,938 barrels; S.D. wood turpentine 161,161 barrels; D.D. wood turpentine 7,161 barrels; sulfate wood turpentine 54,081 barrels (1 barrel = 50 gallons).

⁹ For picture of Havg tanks used, see Chapter 45.

Gum rosin has already been described; wood rosin is the rosin extracted by solvents from the wood residue after the steam distillation of stumps ("lightwood"). Over the same crop year there were produced: gum rosin, 18,413 barrels; reclaimed (gum) rosin 25,226 barrels; wood rosin 973,226 barrels (1 barrel = 500 pounds gross). (From Naval Stores Reports, Dept. Agric.) Some of the uses of rosin are given in Chapters 34 and 35.

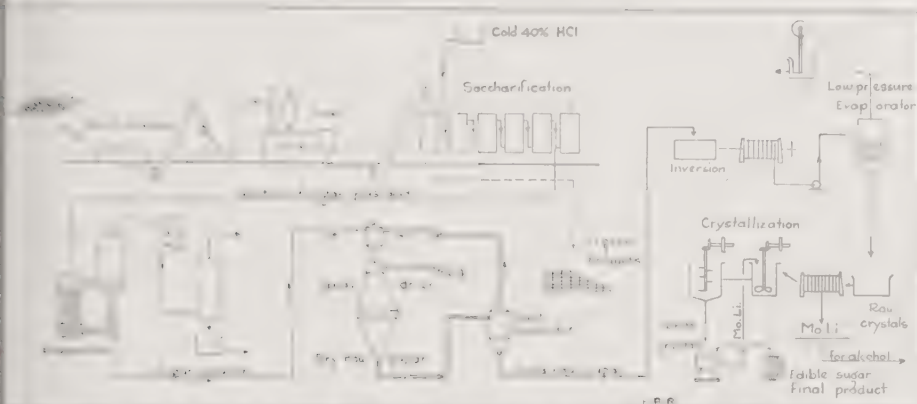


FIGURE 106. Diagrammatic flow sheet for the Bergius wood hydrolysis process.

Pine oil is produced along with turpentine, pine tar, tall oils, and the wood naphtha, from the oil distillate of the wood; in 1939, there were produced 5,198,696 gallons of pine oil valued at 49.2 cents a gallon. (Bureau of the Census.)

Sulfate wood turpentine is the condensate, other than water, of the vapors periodically emitted from the top of the digesters charged with pine wood chips. The black liquor from the digester contains sulfate wood rosin, called "liquid" rosin, a mixture of fatty and resin acids; over the same crop year, there were produced 18,358 tons of liquid rosin equivalent to 10 tons of abietic acid.

Prices for gum turpentine fluctuated between 26.25 and 42.05 cents per gallon in the 1940-41 crop year, and for gum rosin, between 1.43 and 1.85 cents per pound. (From Naval Stores Reports.)

OTHER PATENTS

U. S. Patent 1,792,392, on turpentine, pine oil and rosin from wood rich in oleo-resin by the direct action of strong current of steam to volatilize the oils; 1,772,895, turpentine substitute from pine oil, by adding fuller's earth to pine oil and distilling the steam at a temperature of 125° to 225° C.; 1,740,115, extraction of turpentine oil and rosin from resinous woods, by solvents; 1,859,292, thermal decomposition of wood by subjecting it to direct physical contact and reaction with a highly heated body of hydrocarbons; 1,836,305, wood distillation apparatus; 1,731,242, method of wood distillation; 2,050,235, concentrating acetic acid; 2,034,332, concentrating aqueous acetic acid; 2,177,557, distillation of wood chips.

PROBLEMS

1. A plant using retorts with steel buggies distills 30 cords of beech wood a day for 10 days. What is the total tonnage of charcoal, and how much gas is available per cord?
2. A plant distills every day 200 tons of chipped waste hardwood in continuous process. Consulting the table of products given in text, what are the amounts of each

which are obtained? Make an allowance for the gas required for cleaning the retort and bringing them up to heat.

3. A chipped pine wood contains for each 100 kilograms of dried wood 66 kilograms of reducing sugars, with the composition:

	Per cent
Glucose	60
Mannose	17-21
Galactose	5
Xylose	13
Fructose	1

Allowing the glucose and fructose to ferment without loss to ethyl alcohol, how much of this substance, on the 100 per cent basis, will be obtained?

The same pine chips give per 100 kilograms 2 to 2½ kilograms acetic acid, and 33 kilograms of lignin.

4. A chipped beech wood produces for each 100 kilograms of dried wood 72 kilograms of reducing sugars, with the composition:

	Per cent
Glucose	67
Xylose	28
Other sugars	5

and 25 kilograms lignin, and 6 kilograms acetic acid.

Let the glucose be worked up into a 50 per cent glucose syrup, how much will be obtained per 100 kilograms of wood? Let the remaining sugars be made into caustic feed, what is the weight they will contribute, assuming none is lost? With the acetic production as given, how many pounds of acetic acid would be obtained from a cord of this same wood? (the weight of wood per cord given in the chapter text must be taken as applying).

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"Naval Stores," 1919-1939," Dr. Eldon Van Romaine, *Chemical Industries*, September, October, 1939.

The electric furnace is a comparatively modern device, until its advent the highest temperature commercially available was the white heat of a hot metal burning under forced draft, which gives about 1400°C . In electric furnaces, a temperature three times as high is obtainable, about 4000°C ; this is not so very far from the estimated temperature of the sun's surface, 6000°C . That the high temperature of the electric furnace had made possible the manufacture of products hitherto unknown, known only in the natural state, is not surprising. Important among these are artificial graphite, silicon carbide, aluminum oxide, calcium carbide, and certain alloys.

Chapter 17

Products of the Electrothermal Furnace

There are three main types of electric furnaces, the arc furnace, the resistance furnace, and the induction furnace. In the arc furnace, the heat of the arc is utilized, with perhaps an electrical effect in the case of electrolysis. In the resistance furnace, no arc is formed, but the electrical energy is entirely transformed into heat or thermal energy. If the material furnishing the resistance is the charge itself, the resistance furnace is said to be direct heating. If a material is added purposely for the sake of the resistance it furnishes, without being part of the reacting charge, the furnace is said to have indirect heating. The induction furnace is applied only to metals; it is because of this fact, that if an alternating current of high frequency is passed through a coil of many turns (primary) in the center of which a soft iron core is situated, an alternating magnetic field is formed. A single iron ring (secondary) placed around the first coil and core will become red hot in a few minutes. In addition to these three types, some furnaces involve a combination of two types. Any of these furnaces may be termed electrothermal, for their value lies in the heat they furnish, and the heat has its source in electrical energy. The materials produced in an electrothermal furnace could not be made by means of heat from any other source; it is the high degree of heat which is essential. At the present time no other means for the production of such high temperatures is known. The size of the furnace does not matter; a small furnace a few inches in size is as truly an electric furnace as the large furnace for artificial graphite, 30 feet long.

ARTIFICIAL GRAPHITE

Artificial graphite is made in an electrothermal furnace with direct heating. When coke is heated to the very high temperature which this furnace affords, a change takes place, at the end of which the ash is volatilized as well as any other ordinarily more volatile impurities, and there is left only carbon in the form of graphite. The content of the ash acts as the graphitizing agent; it forms carbides with the coke; later the carbides decompose, and the carbon is left in the form of graphite. The graphitizing must be done in the absence of air; this is accomplished by covering the heated material with a sand mixture.

Certain materials are added to the coke in order to produce shapable pieces, for example, electrodes for electric furnaces and for electrolytic cells; it is these electrodes particularly which have made this industry indispensable one. Graphite is a good conductor of electricity; coke is a poor one.

ELECTRODES FOR ELECTRIC FURNACES

The raw materials for artificial graphite are: calcined petroleum coke, the residue from the distillation of certain crude oils for gasoline; coal-pitch, and a petroleum distillate called black-summer oil. A portion of the coke is powdered in a Raymond mill to such fineness that 60 per cent passes through a 200-mesh screen¹; another portion of the coke is crushed

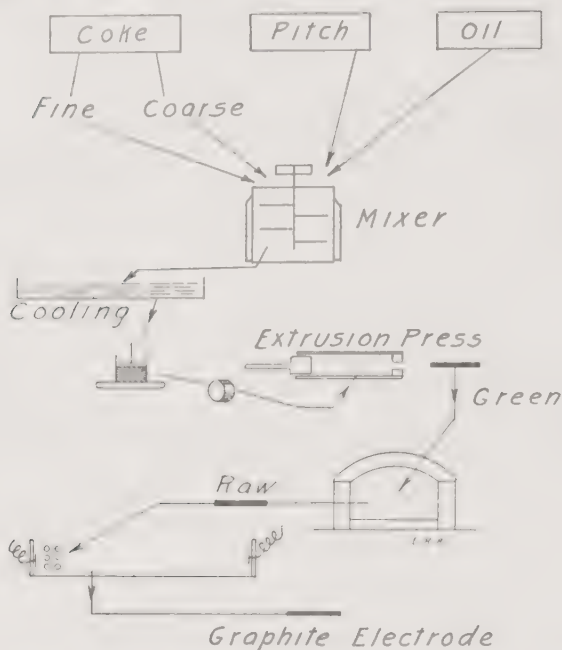


FIGURE 107.—Flow sheet for graphite electrode.

in a swing-hammer mill to a coarse powder. These two sizes are mixed with pitch and oil in steam-jacketed mixers for a period varying from 20 minutes to an hour.² The charge is dumped onto the floor and allowed to cool to 95° C. (203° F.); it is then shoveled to a chute feeding a cylindrical form open at both ends, and placed on a movable table, so that the form may be brought under a ram which presses the soft mass into a cake 16 inches in diameter and 10 inches high, weighing 60 to 70 pounds. The cakes are fed at intervals to an extrusion press, enough cakes being used to fill it. The press is merely a steam-jacketed cylinder of 17-inch internal bore, fitted at one end with a steam-heated die which may be changed to suit the order at the other end with a hydraulically driven piston. The mass is extruded through the die, very slowly, onto a receiving plate. The diameter of the electrode is fixed by the die opening; the length is measured on a stick, and cut off with a wire, as cheese would be. Two men operate the extrusion end of the press; one operates the valves.

¹ Chapter 41. The production of petroleum coke in 1940 was 1,526,600 tons (U. S.).

² The different sizes of coke are used in order to obtain minimum voids.

The pieces, now called the "green" electrodes, are lowered to the floor and led away in shallow troughs with 2 inches of water, and under a spray of cold water. By reason of this cooling, the soft mass becomes comparatively stiff; the green electrodes are now ready for firing. The amount of agglomeration is reflected in the specific gravity: the 16-inch cake has a specific gravity of 1.3; the green electrode, 1.7.

First Baking, producing Raw Electrodes. A first baking is done at a temperature of not over 1100°C . (2012°F .), producing a hard substance with a metallic ring. This may be done in the electric furnace, and may be followed without repacking by the graphitizing heat, merely by changing to a low transformer to a high one; but it is found more economical to perform the first baking in coal-fired kilns with removable arches. The kilns are of such size that for electrodes 4 inches in diameter (circular) and 40 inches long, 500 may be baked at one time in one kiln. The electrodes are packed in sand, preferably re-used sand, so that they do not touch each other, and are well covered so that the fire gases which pass over the top do not come in contact with them. The fire gases pass over the charge, over the sides and rear, and under the floor of the kiln by means of suitable tunnels and cross walls in the brickwork, before they can escape to the stack. A pyrometer³ reaches into the sand; another is placed in the fire gases. The temperature is raised slowly, 5°C . per hour, requiring 5 to 7 days; when 800°C . (1472°F .) is reached, all danger of forming blow-holes is over and the fire is forced until the pyrometer in the sand registers 1100°C . (2012°F .); this heat is maintained for 2 to 3 days.

The charge is cooled slowly; first the arch is removed by an overhead traveling crane; after a day, some of the sand blanket is removed; on subsequent days more is removed until all the sand is finally taken off. The cold charge is unpacked, and the raw electrodes are ready for the graphitizing heat. The gradual cooling is necessary as the electrodes would take fire if they could reach them while they were still hot.

During the baking, there is a loss in weight of 13 per cent and a shrinkage in length of 1 per cent. The green electrode, 4 by 40 inches, weighs 29 pounds.

Graphitizing the Raw Electrodes. The raw electrodes are changed from a hard body to one so soft that it may be cut with a pocket knife, in an electric furnace in which the charge itself forms the resistance to the electric current. The heat attained in the furnace is about 4100°C . (7366°F .), whereas the maximum heat which the coal-fired kiln affords is 1400°C . (2552°F .). The furnace consists of a bed of concrete flags supported on brick piers placed close together, and of two upright end pieces, also of concrete. The length is 30 feet, from upright to upright; the width is 13 feet; there are no stationary side walls. When fully charged the height of the bed is about 6 feet.

The end pieces are provided with openings to receive the stationary graphite blocks forming the terminal electrodes for the furnace; each end piece has eight carbon blocks, 6 inches square, in cross-section, long enough to protrude 2 inches within the furnace and to extend 6 inches outside

³ Chapter 46.

for connection to the copper leads. The connection to the graph terminals is kept cold by a stream of water.

The charge of raw electrodes is packed between the end pieces and placing ground coke over the floor of the furnace to a height of 4 inches the electrodes are placed crosswise to the long axis of the furnace. They are piled exactly over each other, touching, and the vertical rows are separated by strips of wood, replaced by ground coke when the packing is completed. The total weight of the charge is 30,000 to 35,000 pounds. Along the two sides a layer of coke 3 inches thick is placed reaching from one upright end piece to the other; it is held in place temporarily by a steel apron. A layer of coke is similarly placed over the top. It is through these layers that the current passes at the start, for the raw electrodes are poorer conductors than the coke. The graphite terminals at the end walls are buried in the crushed coke and through it make contact with the electrodes nearest them.

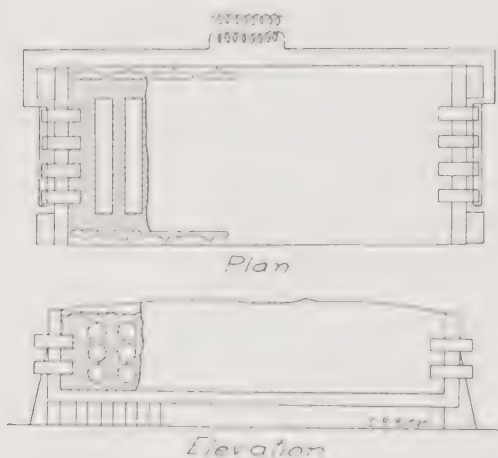


FIGURE 108.—Plan and elevation of artificial graphite furnace for electrodes.

Over the top a layer of mixed sand, coke, and sawdust is spread, to act as a heat-retaining cover; sand previously used, partly converted to silic carbide, is preferred to new sand. Along the sides concrete blocks 4 feet high are set up at a distance of 12 inches from the 3-inch coke layer, and the space so formed is filled with used sand. The electrodes are now buried in crushed coke and protected from the air on all sides; the furnace is ready for the heat.

The current at Niagara Falls is 25-cycle⁴ alternating current; the voltage at the beginning is 240 volts; as the heating progresses the charcoal becomes more conductive, and the voltage may be dropped gradually; at the end it is 30 volts. The electrical load is 1600 kilowatts at the start and at the end, 1200 kilowatts; the latter load is in the form of 40,000 amperes at 30 volts. The current from the hydroelectric power plants is delivered at 12,000-volt current and transformed to the lower voltage in oil transformer; it is brought to the graphite block terminals by means of eight copper bars 4 inches wide and three-eighths of an inch thick.

⁴ 25 cycles per second.

the heating progresses gas escapes from the charge and burns. Promoters are used for the first few days (they are removed as they themselves would be vitrified). The final graphitizing current is on the furnace for three days. After the current is shut off, the furnace is allowed to run six days (for the largest pieces); it is then unloaded. The cycle from one unloading to the next is one month for each furnace. Graphite electrodes may be machined (threaded, for instance) so that even short, the butt ends may be screwed onto the next new piece and threaded. Electrodes of all kinds are made, of square and rectangular section as well as circular.

The *Söderberg electrode* is a continuous electrode for use in fused electrolysis. It is continuously formed and baked above the furnace, and lowered at a proper rate so as to make the same contact. It consists of a metal cylinder or other metal shape suspended above the furnace with numerous perforations to allow gases to escape; a mixture similar to that for other electrodes already discussed is fed in batches to the cylinder. The heat of the furnace bakes the electrode as it approaches the hot zone. Cylinder electrodes are consumed as the electrolysis progresses; a new section is fed on top of the cylinder as becomes necessary. The electrical contacts are made to the outer casing as the unit is lowered, so that current is fed in at the top. The Söderberg electrode makes continuous operation possible, reduces the cost of electrodes, and permits the use of enclosed furnaces.

The electrode has been applied to aluminum electrolytic furnaces with results made of aluminum. The gases from the closed furnace are absorbed in an alkaline solution, and a good portion of the fluoride which escapes from the cell is recovered. The Söderberg electrode has been applied successfully to the Hall process for refining bauxite, and to other types of electrolytic cells.

Graphite powder is made by filling the furnace with coarsely powdered graphite with a central core of 2-inch square graphite rodding, then proceeding as before. Such "bulk graphite" is powdered in a special mill and finds application in the electroplating industry, in dry batteries or cells,⁵ and in lubrication. Mixed with grease it becomes a special lubricant.⁶

Certain articles are baked only a short time, and are semi-graphitized; for example, electric motor brushes.

Artificial graphite is artificial only in the sense that it is manufactured rather than that found in nature; it is purer and more uniform than the natural material. Its higher purity makes it a better conductor and a superior refractory. For all uses except the manufacture of clay-graphite crucibles, manufactured graphite excels the natural. The superiority of the latter in making graphite crucibles is due to the presence of mica fragments which prevent the rapid burning which manufactured graphite would permit; these pieces furthermore offer points of attachment for the clay binder.

A dry cell consists of a central "raw" carbon rod surrounded by a mix of graphite and manganese dioxide as depolarizers; these are contained in a paper bag, which sets in a mix of starch paste, zinc chloride, and zinc chloride, surrounded by a zinc cylinder which forms the second pole; the carbon rod is the positive pole. This is discussed under lubricants, Chapter 24.

ABRASIVES

Silicon Carbide. In the same kind of electric furnace in which graphite, the softest solid known, is produced, silicon carbide, practically as hard as diamond (the hardest substance known) is also produced; but where the graphite furnace the heat-producing resistance is that of the electrodes themselves, in the silicon carbide furnace a central core of carbon furnishes the needed resistance, and the materials which are to be transformed are heated around it. Hence the silicon carbide furnace belongs to the class of resistance furnaces with indirect heating. It is important to note that the temperature of the graphite furnace is much higher than the decomposition temperature of silicon carbide, so that none of the hard substance can exist in the soft graphite.

Silicon carbide, or silicide of carbon, SiC , was unknown before the development of the electric furnace.⁷ Its great value lies in its hardness, in its property of breaking off to form fresh sharp surfaces. These properties have led to its use as an abrasive. It is used in the form of grinding wheels, grinding powders, and polishing papers. Silicon carbide is sold under the trade names of "Carborundum," "Crysolon," and others.

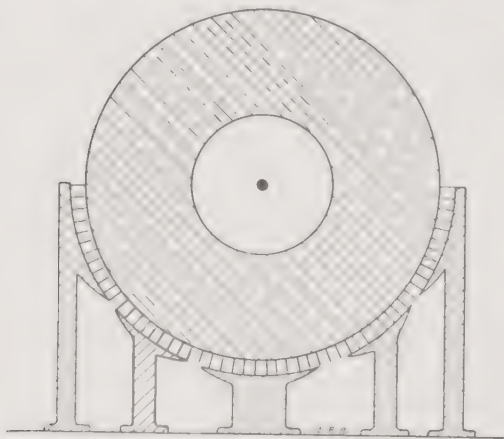


FIGURE 109.—Cross-section of the silicon carbide furnace, showing the central graphite rod surrounded by the core of coke (in blank) and the mixed materials forming the charge proper.

Silicon carbide is made in furnaces 40 feet long, 7 feet wide and 6 feet high. The charge itself and the heating core form the greater part of the furnace; the permanent portion is only the bed and the two upright end walls in which the electrodes are imbedded. The bed of the furnace consists of curved cast-iron pieces lined with hard firebricks, on which the charge rests. The materials for the charge are made up in the proportions of 100 parts of the finest grade glass sand, 60 parts of coke, and 10 parts of sawdust (all by weight). These ingredients are thoroughly mixed and loaded from a bucket carried on an overhead crane; the bucket is filled from a bin on the upper floor, by gravity.

The manner of loading the furnace is as follows: Enough material is charged to reach half-way of the height of the total load; a long furrow 2 to 3 feet wide running from one end wall to the other is then made in the center of the charge, filled with crushed coke, and a 2-inch graphite rod⁸ reaching

⁷ The experimental work was done at Monongahela City, Pa., by E. C. Acheson.

⁸ Made in the same way and from the same mass as the graphite electrodes.

ole length of the furnace is laid in the middle. The core widens at the walls so that all the graphite terminals are in contact with the coke when runs without a break to the opposite wall. Next enough coke is added to complete the core, and then the remainder of the mixed charge. The furnace is then ready for the current. A portion of the charge remains moist and forms the blanket required to keep out the air and to conserve the heat.

The electrical load is 1500 kilowatts, and is continued until a total of 10 kilowatt hours has been applied. The current is alternating (25 at Niagara Falls), the voltage is 300 volts at first, 200 volts at the end. The period of heating is about 36 hours, and the maximum temperature is 600° C. (4624° F.) in the reacting mass.⁹ Blue flames are visible all over the mass for the greater part of the heating; they consist of carbon oxide, escaping and burning. Toward the end, these flames turn yellow, and sodium compounds begin to volatilize and pass out. The furnace is allowed to cool and is then opened. The inner part of the mixed charge is found to have been transformed into large hard chunks consisting of single, well-formed, flat crystals of various colors; some regions have a velvety violet color, others are green-bronze to light green, others are colorless. The color cannot be foretold or regulated; for the manufacturer this is of no importance and perhaps of no interest, but to the visitor the newly opened furnace is a beautiful sight. The crystals are hard, with sharp edges, forming jagged peaks which jut out from the mass.

The desired product forms the inner part of the mixed charge, adjacent to the carbon core, so that moving from the edge inward, there is met first the mixed charge, the silicon carbide crystal layer; next some graphite in the shape of the silicide crystals, because the crystals first formed their silicon by overheat; finally the inner core, now partly graphite. From 64,000 pounds of mixed charge, about 16,000 pounds of silicon carbide crystals are obtained. The graphite in the center is a by-product; most of it is sold to electrode makers. The cycle from unloading to unloading takes a week.

The function of the sawdust is to make the mass porous so that gases can pass out. It will be noted that enough coke is added to remove the oxygen from the sand in addition to the amount required to form the silicide. The reaction is $\text{SiO}_2 + 3\text{C} = 2\text{CO} + \text{SiC}$.

Silicon Carbide Products. The chunks removed from the furnace are first stored in the yard, in heaps which again form a striking sight, especially on a sunny day. When needed, the chunks are crushed in steel edge-runners, the pans of which revolve while the corrugated steel wheels are stationary. The crushed crystals are washed in water, boiled in sulfuric acid and later in caustic soda, dried, then sieved, the finer crystals on long narrow screens which move forward with a slow motion, backward with a fast motion. Coarse crystals are made into large wheels (10 to 36 inches in diameter); smaller crystals are for small wheels.¹⁰ There is an infinite

⁹ "Temperature measurements in commercial silicon carbide furnaces," by Raymond R. Ridgway, *Electrochem. Soc.*, 61, 217 (1932).

¹⁰ The sizes of particles are also varied in any given-sized wheel according to the degree of smoothness desired.

variety of sizes and shapes. Crystals which pass a 50-mesh screen are ground to a rather coarse grinding powder; those that pass a 150-mesh screen to a fine one. A large percentage of dust is unavoidably produced, which has little value as an abrasive; it is used in the refining of steels. Grinding wheels and tips for dental instruments form a considerable outlet. Grinding wheels for automobile valves, for instance, are silicon carbide powder of two sizes, set in a calcium soap jelly. Cloth and paper coated with emery are extremely efficient and replace to a great extent the older emery cloth and sand paper. Honing stones and sharpening tools for farm implements are in a ready market.

In order to make grinding wheels, the crystals are mixed with a thin clay containing powdered feldspar and flint, to form the approximate shape; and after drying, the correct shape and size are made by trimming with power-driven knives. The wheel is then ready for firing; this is done in coal-firing kilns, similar to those used in potteries.¹¹ The temperature is controlled by means of pyrometric or Seger cones and by the color and length of the flame. The baking requires 10 days; the complete cycle is 14 days for a wheel. After firing, the wheel is inspected, tested by spinning it at a rate in excess of the stated working rate, and if passed, is then ready for shipment. Instead of clay, a binder of rubber, or of synthetic resin, is used, with excellent success. Silicon carbide wheels, stones, and cloths are black or gray. Products which have similar uses are made from fused aluminum oxide, obtained by firing bauxite; these products are yellow.

Electro-orientation.^{11a} In the manufacture of so-called sand paper, in which may have sand, silicon carbide, or some other artificial abrasive, the deposition of the abrasive grains onto the paper or cloth backing is controlled under the influence of electrostatic charges, with the result that all the grains adhere to their backings with their sharpest point uppermost. Further, the grains are more evenly spaced. The joint result of these improvements is to give the abrasive paper about 35 per cent increased cutting quality. In the course of application the particles are charged with high-voltage electricity, and move from one electrode to the other, rotating, so that their longest or longer dimensions are parallel to the direction of force; hence, the method of seating. Particles so charged repel one another equally, and this leads to equal spacing. The potential applied is 100,000 volts.¹²

It might be remarked in passing that coarse sand paper has 12,000 grains per square inch, whereas fine sand paper has up to 35 million.

Fused Aluminum Oxide. Another artificial abrasive which is made with the help of the electric furnace is artificial emery, a crystalline aluminum oxide (Al_2O_3), known in the trade under the names of "Alundum" and "Alundite."^{12a} The naturally occurring crystalline alumina is corundum, which may be transparent and blue (sapphire) or red (ruby); when less pure it is colored brown or black, it is emery. Its hardness is 9 on the scale on which diamond is 10 and graphite 1. Its value as an abrasive is high; the yearly tonnage is about five times the tonnage of the silicon carbide (for 1

¹¹ Chapter 10.

^{11a} A branch of Applied Electrokinetics.

¹² "Electrocoating sand paper—a method for procuring increased abrasiveness," *The Electrochemical Reviews*, 113, 121 (1936).

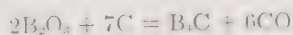
^{12a} Also diamantin, electrit, lionite, exolon.

States and Canada). Artificial emery contains about 95 per cent α ; its color varies from white to yellow and brown.

Aluminum is made from bauxite, a hydrated alumina which contains α in amounts varying from 1 to 20 per cent; it also contains some iron and other impurities (ferrosilicon). The bauxite is first calcined, then mixed with fine coke and iron borings in amounts depending on the silicon content, and subjected to the heat of a combined arc and resistance furnace. A furnace of 21,000 pounds may consist for example of 73 per cent bauxite, 25 per cent fines, 3 per cent coke, and 2 per cent iron; the bauxite is (here) 90 per cent pure. This furnace, one of a bank of eight, is circular, 6 feet diameter, and consists of a water-cooled steel shell lined with a wall of α (removable) and fitted with a carbon hearth; two suspended electrodes with single-phase current furnish the heat. The furnace is 7 or 8 feet diameter and 5 feet deep; the operation is intermittent. As the melting progresses the furnace receives more of the charge until finally it is full. The electrodes are hung by a cable which is wound on a drum. They constantly move up and down, a correcting action which keeps the current through the furnace constant. If the electrodes dip low, more current flows; the greater current actuates a motor, raising its speed, which is translated mechanically into an up-and-down motion. Too little dip means less current and a lower speed. As the electrodes wear, the cable automatically lowers them. To some extent a separation takes place; the ferrous impurities (ferro-silicon) settle to the bottom, the fused alumina on top. The furnace is cooled, the removable wall lifted out, which is done by a crane to lift out the ingot, weighing about 10 tons. The cycle for one furnace is 24 hours; the current 130 volts and 500 kilowatts; the electrodes are carbon. The mass is broken, sorted, crushed, washed, and refined by chemical treatment; it is made into wheels, sharpening stones, grinding powders by methods similar to those which have been described for silicon carbide. A considerable portion of the product serves to make artificial emeries, in brick and other shapes.

Pure white and chemically pure alumina crystallized in the electric furnace is also made, in fact to the extent of 10 per cent of the total crystalline alumina production. It is made from pure alumina (purified by the electrolytic process, see Chapter 18) with no addition of carbon, and with graphite electrodes in the furnace. Wheels made from this white alumina grind iron.

Boron carbide. Boron carbide, a comparative newcomer, is made by heating boron oxide with carbon in an electric furnace ^{12b} to a temperature of 2000° C. (4352° F.):



The product is harder than tungsten carbide, silicon-carbide, and crystallized diamond. It is black, and has a glass-like fracture. In powder or grain form, it serves as an abrasive for special purposes; its main use at the present time is in its molded form. When heated to a high temperature and a high pressure, the powder forms a block, with the shape of the

^{12b} U. S. Patent 1,897,214, to Raymond R. Ridgway.

mold; the boron carbide liquefies enough to be self-bonding. The nozzle and blasting equipment are made of this molded boron carbide to save weight.^{12c}

TABLE 33.—*Artificial abrasive products, 1939 (U. S.).*

Artificial abrasives	
Grinding wheels	\$29,436,500
Abrasive papers	9,028,252
Abrasive cloth	7,427,431
Abrasive grains	8,744,055
Total artificial abrasive products	<u>\$71,519,177</u>

Bureau of the Census.

CALCIUM CARBIDE

To the development of the electric furnace is due another substance which was not known before, namely, calcium carbide. It is formed by lime and coke mixed and heated to a temperature of 2000° C. (3632° F.) or higher. Calcium carbide, CaC_2 , is important chiefly because with water it forms acetylene, used for lighting and for the steel-cutting and welding torch, but in addition it forms the starting point for one of the several methods of fixing atmospheric nitrogen (cyanamid).¹³ It was in this respect that it became of paramount interest to the public in the emergency of 1918; a plant was constructed at Muscle Shoals, Alabama, which contained very large furnaces.^{13a} The carbide furnaces fall in

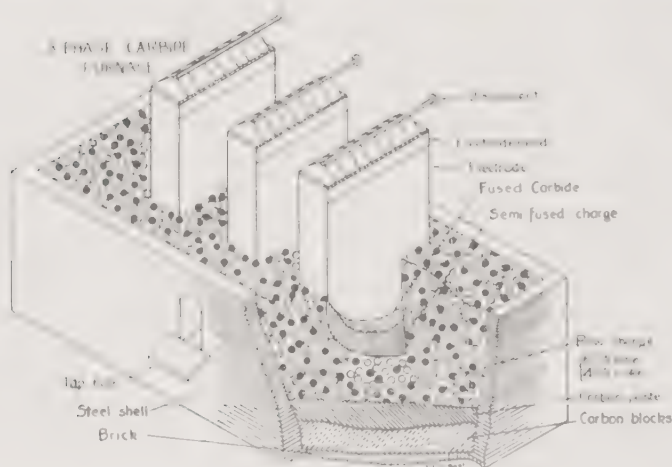


FIGURE 110.—A carbide furnace, with three electrodes, and an electric circuit. The product is tapped from the top, and the operation is continuous (Based on a sketch due to the American Cyanamid Co., New York.)

class of combined resistance and direct-arc heating, that is, some of the heat is due to the resistance of the raw materials and product to the passage of the current, but most of it is due to sparking across the charge.

A modern carbide furnace is shown in Figure 110; the long dimensions may be 30 feet or more. The charge is 60 per cent lime, CaO , and 40 per cent

^{12c} Trade names for boron carbide are Norbide, Borolon, and others.

¹³ Chapter 6.

^{13a} The intention was to make calcium carbide, then calcium cyanamide, then by the action of steam in autoclaves on the cyanamide, ammonia. This latter was then to be oxidized catalytically to nitric acid made. The acid after concentration to 100 per cent was then to be used for the manufacture of cellulose for munitions. In peace time, the acid would serve to make sodium and calcium nitrates which are fertilizer materials. The war ended before the plant could be put in operation. Since the power plant is a distinct and separate consideration.

The current is applied through three suspended graphite electrodes, which are adjustable; an idle electrode is formed by the layer of carbon at the bottom. The reaction is $\text{CaO} + 3\text{C} = \text{CaC}_2 + \text{CO}$; the carbon monoxide evolved was wasted at one time, but is now frequently saved for other reactions. The calcium carbide is produced in the form of a melt, tapped continuously. No refractory except carbon will withstand a carbide. It is customary, therefore, to build the furnaces very strong and to depend upon a thick layer of semi-fused material as the working lining of the furnace. In consequence, the active part of the furnace is only a small zone immediately surrounding the electrodes; the charge is only a very few tons.

The raw materials, limestone and coke or coal, must be carefully selected, especially if the carbide is to be used for acetylene production. The limestone should contain practically no phosphates, for these form phosphides which on burning leave a white deposit; it must be free from iron carbonate, for magnesium does not form a carbide and the presence of its oxide in the charge causes a waste of current. The coke is selected, washed free of dust, selected further for low ash (3 per cent is low); anthracite is used in England to some extent. Were no selection made, it might well happen that the carbide would be so viscous, because of impurities, that it would not flow.

The liquid carbide flows into "chill cars" of 1000 pounds capacity; the carbide contracts on cooling, so that it is readily dumped. If it is intended for acetylene production, it passes through a jaw crusher¹⁴, and then through very slow rolls¹⁴ to give a minimum of dust; the pieces are screened to give 2-inch pieces for large generating tanks, pea-sized for miners' lamps. For making cyanide, the crushed carbide is sent through a conchoidal pebble mill, which gives a powder, 80 per cent of which passes a 20-mesh screen; this then is fed to a tube mill¹⁴ (pebbles), which gives "fine" carbide, 85 per cent of which passes a 200-mesh screen. To remove the possibility of forming an explosive mixture from acetylene, generated by the carbide, and to remove accidental moisture, with air, the grinding is done in an atmosphere of nitrogen.

The crude carbide is 83 per cent CaC_2 , 14 per cent lime (CaO), and 3 per cent carbon; it contains small amounts of silicides, phosphides, and other impurities. It will be evident that the raw materials must be carefully selected, for it is remembered that there is no slag which can be rejected; whatever impurities enter the furnace, and are not volatilized, will appear in the carbide.

The electrodes wear away during operation, and the merits of the several types of furnaces must include a reasonably low carbon consumption; in the type described above, it is 70 pounds per ton of carbide.

Another important figure is the number of pounds of carbide produced per kilowatt-hour consumed; from the figures given for this furnace it is 2.3 pounds per kilowatt-hour for 1 pound of crude carbide; or 4.3 kilowatt-hours for 1 pound of crude carbide; expressed still differently, it is 9.2 pounds of product per kilowatt-hour. The current efficiency is then about 62 per cent.

OTHER PRODUCTS OF THE ELECTROTHERMAL FURNACE

The ferro-alloys are described in Chapter 48.

Carbon disulfide is a product (but not exclusively) of an electrothermal furnace of shaft-like construction¹⁵; the materials are charcoal and sulfur; the charcoal is fed from the top, and is swept by the outgoing vapors of the product; the sulfur is fed through channels in the walls to the base of the furnace. The electrodes are placed just above the hearth, and the heat is due to the resistance of the charcoal to the passage of the current; it is therefore a resistance furnace with direct heating. The vapors are condensed by cold water and the liquid redistilled. Furnaces in which fuel gas is applied are also in successful use. Carbon disulfide is flammable and, with air in certain proportions, explosive; the furnace operates smoothly, however. The product is of value as a solvent; it is used to dissolve carbon tetrachloride, and in the vulcanization of rubber¹⁶; but its important use is in the manufacture of viscose silk or rayon.¹⁷

An electrothermal furnace has been described (1932) which recycles sulfur vaporized in a separate lower chamber. The furnace proper or upper chamber has 2 electrodes; the carbon is fed as charcoal with a small amount of broken hard graphite pieces introduced just over the electrodes in order to lower the resistance. The carbon mass is kept at red heat.¹⁸

Tremendous amounts of carbon disulfide, however, are also made in an electrothermal furnace, with the retorts heated by the more common fuels. Production by all methods was 161,523,747 pounds of carbon bisulfide, valued at 3.22 cents a pound (1940, U. S.).

OTHER PATENTS

U. S. Patent 1,859,856, production of silicon carbide by charging a mixture of calcium silicate slag containing 85 per cent combined CaO and SiO₂ and carbonaceous material into an arc type furnace; 1,872,202, on making calcium carbide, by forming briquets of coke, lime, and water, drying and smelting them with additions of lime or coke; 1,705,697, 1,705,717, resistance type furnace; 1,737,566, electric furnace for production of carbon bisulfide; 1,979,052, electric resistance furnace; 2,005,956, method of making abrasive metal carbides, and apparatus; 1,893,106, method and apparatus for electrically fusing nonconducting materials.

PROBLEMS

1. The charge for a furnace run for making silicon carbide is 32 tons of materials, coke, sand, and sawdust, in the proportions specified in the text. 10 pounds of crystals of silicon carbide are obtained. Let the sand be 98 per cent SiO₂. What percentage of the total possible product is the amount actually collected?
2. A calcium carbide furnace produces 48 tons of crude carbide, 85 per cent C₂, per day. The current is 130 volts, 60,000 amperes. Find the kilowatt hours for production of crude carbide, and for a pound of 100 per cent material. What is the horsepower-day per pound? Use the appendix for conversion figures.
3. What is the yield of carbide in Problem 2 on the basis of the lime used, if the lime is 97 per cent CaO?
4. The heat effect in the formation of calcium carbide is included in the reaction below:



Changing these to kilowatt hours gives a theoretical energy consumption of 1.25 kwhr. per kilo of CaC₂. This is on the basis of 100 per cent current efficiency.

¹⁵ "The manufacture of carbon bisulfide," by E. R. Taylor, the inventor of the process, *Ind. Eng. Chem.*, **4**, 557-9 (1912).

¹⁶ Chapter 39.

¹⁷ Chapter 22.

¹⁸ U. S. Patent 1,849,140.

silicon carbide. It also rises to room temperature, while in position. The reaction takes place at about 2000° C., necessitating a higher consumption of current and gas, and making up for heat losses by radiation. At 50 per cent efficiency the figure becomes 3.92 kw/hr. per ton of product. The consumption in the text is somewhat higher. Check all these figures; 1 kw/hr. = 860.5 Calories (about) = 1 kilogram calorie = 1000 gram calories, which figure should also be used by the student.

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In contrast to electrolytic decompositions at room temperature, in solutions, similar decompositions may be brought about by electric current at high temperatures, in a bath of fused salts; such an electrolytic cell then will be called an electrolytic furnace. It is by means of such a furnace that all our aluminum is prepared, and it is on aluminum, fabricated into aircraft, that the safety of the nation depends. A debt is owed to the pioneering manufacturer who kept the commercial processes going in the days when he had to look about for possible uses for his new metal in order to make sales.

Chapter 18

Products of the Electrolytic Furnace (Aluminum, Magnesium, Sodium) and Products of the Electrolytic Cell Other than Caustic

The decomposition of salt in water solution, resulting in the formation of caustic soda and chlorine, by passing direct current through the cell, is the most familiar instance of electrolytic decompositions.¹ Fused salts, freed from water, at temperatures which may be red heat and higher, are similarly decomposed. The attempt to treat fused sodium chloride in that way resulted in failure until the advent of the Downs cell. The electrolytic decomposition of aluminum oxide dissolved in fused cryolite ($\text{AlF}_3 \cdot 3\text{NaF}$) has been completely successful and constitutes the present method for the manufacture of aluminum metal; a similar process serves for magnesium. The electrolysis of fused salt is the modern method of manufacturing sodium metal; its comparatively low price permits its use for the preparation of a number of materials which could not otherwise be made, including sodium peroxide and sodamide.

The three processes just given are straightforward decomposition reactions, by direct electric current; another type of reaction is performed in the electrolytic cell, chiefly with hydrous electrolytes, namely, that of oxidation, at the anode. Examples are the change of sulfuric to persulfuric acid and of manganates to permanganates; these are presented later in this chapter.

ALUMINUM

The electrolytic process for the manufacture of aluminum was invented by an American, Charles M. Hall²; at about the same time, the French inventor Héroult devised essentially the same process. Previously, aluminum had been made by the action of sodium metal on aluminum chloride or sodium aluminum chloride; the cost was high, because sodium at that time was made by reducing sodium hydroxide by means of coal in retorts. The production was small.

¹ Chapter 5.

² Oxidation may also be considered as a partial loss of electrons on the part of a negatively charged ion, at the anode (the plus pole).

³ U. S. Patent 490,766 (1890); the Hall process was made more efficient thermally by the use of the Bradley internally heated furnace. References to the famous litigation which grew out of this circumstance will be found in "The Law of Chemical Patents," Edward Thomas, New York, D. Nostrand Company, 1927.

The principal mineral from which aluminum is electrolytically extracted is bauxite, the hydrated aluminas, $\text{Al}_2\text{O}_3 \cdot \text{H}_2\text{O}$ and $\text{Al}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$. The extraction of aluminum in national defense makes bauxite, its source, an actual war material. Table 34 gives selected production figures.

TABLE 34.—World production of bauxite.*
Selected from 20 items.

	1940	1936
British Guiana	700,000 metric tons	
Hungary	700,000 " "	
France	700,000 " "	
Dutch Guiana (Surinam)	615,434 " "	
Italy	530,000 " "	
United States	445,958 " "	
U. S. S. R.	300,000 " "	
Netherlands Indies	274,345 " "	
Yugoslavia	150,000 " "	
Johore	63,787 " "	
World production	4,627,000 " "	2,829,000 m.t.

* All figures are estimates except those for Dutch Guiana, United States, Netherlands Indies, and From Minerals Yearbook, 1940.

In 1941, the production of bauxite in the United States reached 899,500 tons; the imports similarly were much larger, about 940,000 long tons (1). It is expected that in 1942, the production and importations will be about double.

The material electrolyzed in the furnace is aluminum oxide, Al_2O_3 , dissolved in cryolite, $\text{AlF}_3 \cdot 3\text{NaF}$. The latter is obtained from Greenland where extensive deposits occur (Ivigut), the only commercial deposits in the world. The demand for cryolite has been great enough to permit the manufacture of an artificial cryolite. The aluminum oxide or alumina must be pure; it is made from bauxite by various processes, of which the Bayer process is best known. The Bayer purification process involves fine-grinding of bauxite, followed by digestion with caustic soda solution; the alumina dissolves, the iron oxide and other impurities remain undissolved, as a mud. The suspension is diluted somewhat, filter-pressed or separated in thickener; the clear filtrate or overflow, containing sodium aluminate, $\text{Na}_2\text{Al}_2\text{O}_4$, is treated with precipitated alumina from a previous batch, when about 70 percent of the dissolved alumina precipitates⁴ in the form of coarsely crystalline trihydrate, $\text{Al}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$. This is in turn filtered or thickened and washed; the solid is next dried, calcined, and is then ready for introduction into the electrolytic furnace. The filtrate or overflow is concentrated and used over again.

The Bayer process is best adapted to rich bauxite ore, containing 55 to 60 percent alumina, and low in silica (below 7% SiO_2). Other purification processes are the Hall, the Pedersen, and the Haglund.

The electrolytic furnace in the Hall aluminum process operates at a temperature of about 950°C . (1742°F). It partakes of the character of both electric furnace and of an electrolytic cell; the substantial current employed for electrolysis also generates heat by virtue of the resistance of the electrolyte and cell; hence the furnace must be classed among the

Iron. Met. Eng., 19, 807 (1918).

resistance furnaces with direct heating.⁵ By means of this heat, the electrolyte is maintained in fluid condition and aluminum is electrolytically deposited by the passage of the current.

The furnace or cell consists of a steel shell, the size depending on current capacity. The shell is lined with firebrick or other insulation; this is covered with a baked carbon lining. Steel collector plates attached to the shell and buried in the carbon lining carry the current from the molten metal. (See Fig. 110a). The bottom may be slightly inclined so that the molten

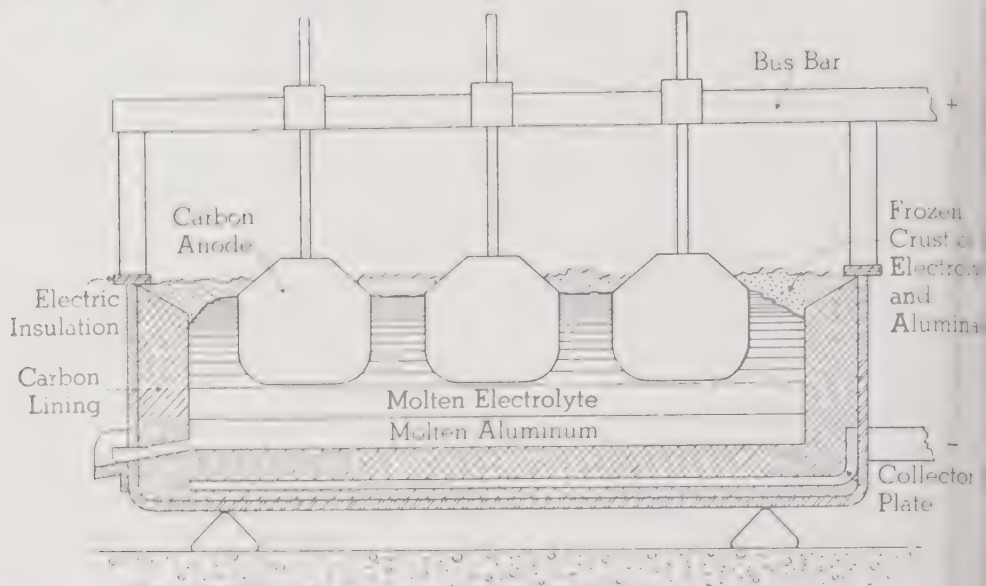
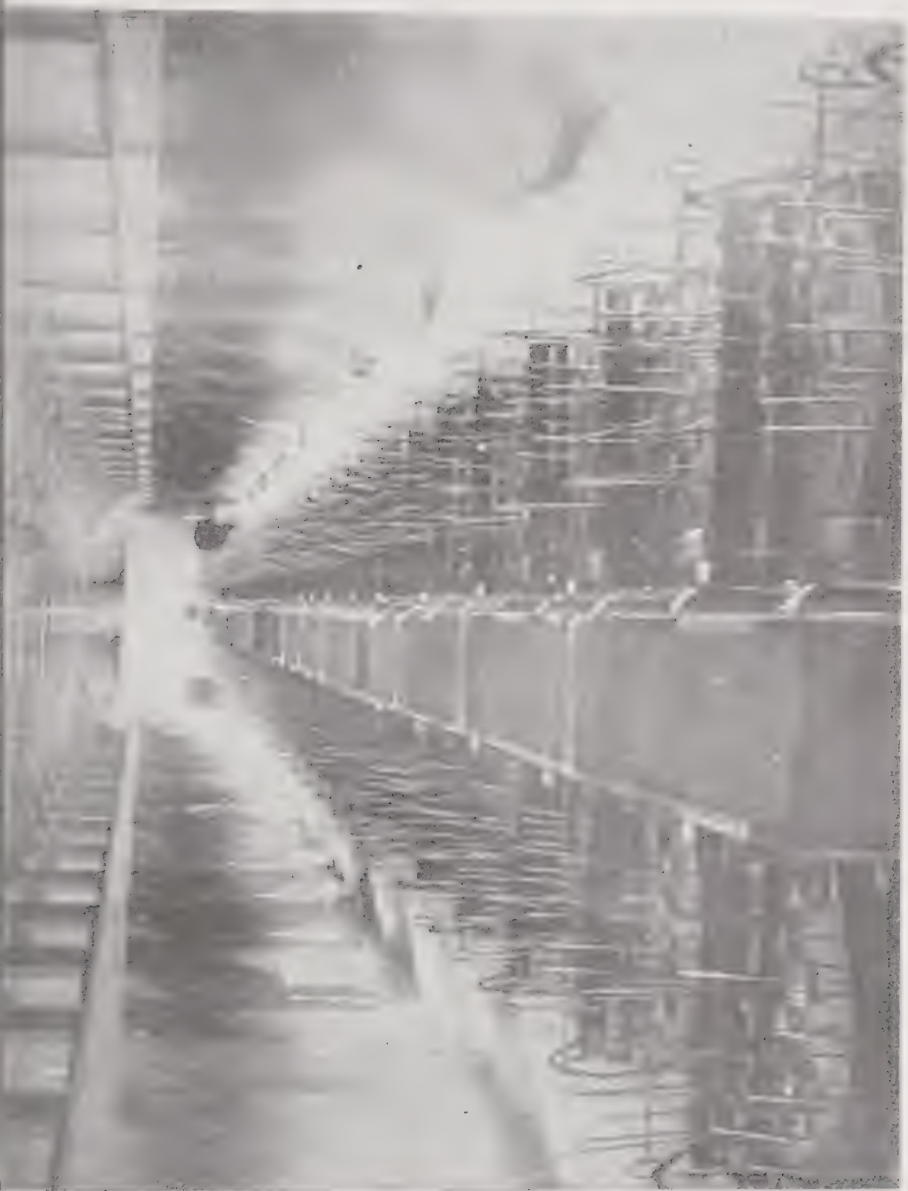


FIGURE 110a.—Cross-section of the electrolytic furnace for making aluminum from alumina in a bath of cryolite. The several parts are labeled. (Compare the view in the picture just following.) (Drawn and kindly supplied by the Aluminum Company of America through Mr. Douglas B. Hobbs.)

metal can be run to a tap hole. The fused cryolite is contained in the carbon-lined cell cavity; the anodes, made of hard carbon, are suspended from above and may be lowered as they are consumed. During operation, the bottom is covered by melted aluminum, which forms the cathode; the anodes are lowered to within about 2 inches of the metal. The number of anodes per cell varies between 4 and 12, arranged in single or double row; they vary in cross-section and are between 6 and 12 inches square. The number of cells varies with the size of the plant; they are usually arranged in banks of 24.

Alumina is added to the fused cryolite at certain intervals; the content of dissolved alumina is usually about 2 to 5 per cent. The added alumina does not at once sink to the bottom, as its higher density would suggest, but remains in the cell bath long enough to dissolve, because agitation of the electrolyte is provided by escaping gas bubbles and by the effect of the electromagnetic field produced by the large currents flowing through bus bars, cell walls and linings. The electrolyte bath is covered with a frozen crust of electrolyte and alumina, so that the surface of the cell presents a white

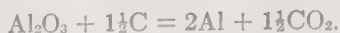
FIGURE 110b.—A view of a row of electrolytic cells or furnaces producing aluminum. Above the anodes and anode rods connected to the bus bars, the hoe lying lengthwise on the cell for spreading the fresh alumina. The vessels into which the metal is tapped are set below the floor just in front of each cell not visible from the camera position. (Compare line drawing just preceding.) (Courtesy of the Aluminum Company of America, Pittsburgh, Pa.)



appearance, with no liquid visible. A certain amount of fluorspar, CaF_2 , is sometimes added to lower the fusion point of the electrolyte. The density of the melted electrolyte must be kept lower than that of the melted aluminum; otherwise the metal does not collect on the bottom.⁶ The reaction is primarily:



but the oxygen attacks the anode, forming carbon dioxide. Hence the reaction is:



The carbon dioxide forms some carbon monoxide at the hot anode, so that the gas evolved contains some 10 to 50 per cent monoxide. The gases pass out through the cryolite to hoods placed above the cells. The decomposition voltage for alumina at 915°C ., dissolved in fused cryolite, and reacting in (2), is 1.55 (see problem 6). The normal drop in voltage per cell is 0.67; a rise indicates that more aluminum is needed. If aluminum becomes dispersed in the cryolite as a metal fog or mist, it may be carried to the anode, there to be oxidized by the atomic oxygen, forming alumina again; the current efficiency⁷ is thereby lowered. This happens to some extent all the time, along with other disturbances, so that a current efficiency of 90 per cent is considered good. The amperage varies with the size of the cell. It may be 8,000 amperes for the small ones, and as much as 40,000 amperes for the large ones. Each cell is tapped once a day, giving for the small cells about 100 pounds of metal per day. The power requirement in the newer cells is as low as 9.5 kwhr per pound of metal. The anode consumption is 0.6 to 0.7 pound per pound of metal. Two pounds of alumina are consumed to make one pound of metal.

Aluminum is prized because of its low density, its resistance to corrosion, its good electrical conductivity, its pleasing color, resembling silver, and its high strength of some of its alloys. These properties have led to numerous uses, such as for the construction of chemical vessels, kitchenware, electrical transmission lines,⁸ architectural applications, and in the transportation industry, on land, sea, and in the air. The one use which now overshadows all others is aircraft construction;⁹ every effort is being made to increase the production of aluminum, while at the same time prohibiting the use of the metal for civilian purposes. It is very likely that after the present war there will be abundant aluminum production capacity, and it may be that great improvements in the equipment of chemical plants will become feasible. Of the chemical uses of aluminum, it may be said that the avidity with which it combines with oxygen at high temperatures has led to its use in deoxidizing Bessemer¹⁰ and open-hearth steel, and in the thermite process.¹⁰

Commercially pure aluminum is generally considered to contain about

⁶ Molten aluminum at 950°C . has density 2.36; solid aluminum, 2.58; fused cryolite (emp. 950°C .) has a density of 2.17; solid cryolite, 2.9.

⁷ Chapter 5.

⁸ There are more than a million miles of aluminum cable transmitting electrical current in the U. S. today.

⁹ A fighter plane requires about 5500 pounds of aluminum for its construction; a medium bomber contains 13,000 pounds of aluminum, and may contain as much as 1000 pounds of magnesium, as 550 pounds of stainless steel and 4000 pounds of alloy steel.

¹⁰ Chapter 48.

cent aluminum with minor proportions of iron and silicon which, in turn, act as alloying additions and give the metal greater strength and stiffness.

The strength of aluminum is greatly increased by alloying with small percentages of other metals, such as copper, magnesium, manganese, silicon, zinc, nickel, and chromium. Certain alloys can be given additional strength by heat treatment. Duralumin is such a "strong alloy;" it contains 4 per cent copper, 0.5 per cent magnesium, 0.5 per cent manganese, and the silicon and iron present in the aluminum as produced in the electrolytic cell. The alloy, in wrought form, is heated to 500° C. (932° F.), rolled, and aged 4 days; the resulting bars have a tensile strength of 60,000 pounds per square inch, equal to that of mild steel. Aluminum and its alloys can be fabricated into many commercial forms such as plate, sheet, foil, bar, rod, tubing, wire, extruded shapes, and made into castings by the sand, permanent-mold, and die-casting processes. Aluminum bronze is an alloy of copper with about 10 per cent aluminum.

The method of purification or refining, known as the Hoopes process, illustrates how small differences in properties may form the basis for successful large-scale operation. An electrolytic bath of fused cryolite, to which certain amounts of barium fluoride are added to adjust the density, is employed in this process. A heavy aluminum alloy forms the bottom layer in the refining cell. A layer of pure aluminum is light enough so that it floats on the top of the heavier electrolyte, forming the cathode upon which the pure aluminum, electrolytically dissolved from the anode layer, is deposited. The impurities stay in the bath. By this process, aluminum of 99.99 per cent purity is produced. As with many other metals, the properties of this high-purity aluminum are quite different from those of the less pure varieties.¹¹

United States production in 1940 was 206,184 tons of aluminum metal; by 1941 it was estimated that new plants installed have raised the installed capacity to 450,000 tons a year. The continued efforts at the present time (February, 1942) will probably lead to an installed capacity of 500,000 tons a year, and the actual production will be about the same. Military requirement is expected to be over 700,000 tons a year.

The price of primary aluminum was 20 cents at the beginning of 1940, and rose to 35 cents at the end. There is, besides the industry producing primary metal, a very extensive business in remelting scrap, producing secondary metal.

MAGNESIUM

Metallic magnesium is made in several ways. One of these is the electrolysis of fused magnesium chloride, usually containing potassium or sodium chloride, which lower the fusion point 718° C. (1325° F.) and are decomposed by the current in the presence of the magnesium salt. The magnesium chloride may be obtained from mother liquors from natural or synthetic brines; or it may be used in the form of fused carnallite. The electrolytic cell consists of a cast-iron vessel, unlined, and set over a fireplace with a gas burner, so that heat may be applied part of the time or all the time.

For further details, see: F. C., "Electrolytic Refining of Aluminum," *Trans. Am. Electrochem. Soc.*, 47, 1 (1925).

Anhydrous carnallite, $\text{MgCl}_2 \cdot \text{KCl}$ and equivalent mixtures melt at 460° (860°F.), and magnesium metal melts at 650°C. (1202°F.). The is operated just above the latter temperature, so that globules of magnesium form which rise to the top of the fused chlorides. The pot is the cathode and is connected metallically to a secondary iron cathode, a cylindrical sleeve surrounding the graphite rod in the center of the melt, the anode. By means of proper construction of the cathode sleeve, a circulation of melt¹² can be set up which aids the rise of the globules; they reach an annular gutter facing downward, set in the melt near its upper surface. The metal is withdrawn from there, after it has cooled enough so that it no longer takes fire when exposed to air. The second product of electrolysis is chlorine; given an anhydrous feed to the cell, the corrosion of the chlorine is reduced, and it is successfully handled. The decomposition voltage for fused magnesium chloride at 700°C. is 3.01; the operating voltage 5 to 6. For the production of 1 pound of metal there are required 4 to 5 pounds of anhydrous magnesium chloride. The anode material is graphite, and the current efficiency is 70 to 80 per cent. It should be noted that when fused carnallite is fed to the cell there is an accumulation of potassium chloride; a periodic removal of the cell bath is necessary.

To the magnesium chloride obtained from mother liquors from brines and from carnallite, there has been added magnesium chloride made from sea water. The salt so produced is then electrolyzed in a cell similar to the one just described. The same company which has produced magnesium for many years from brines at its Michigan plant, the Dow Chemical Company, constructed and operates this new plant at Freeport, Texas. Sea water, containing 0.48 per cent MgCl_2 , is pumped to a flocculator to which a milk of lime made from calcined oyster shells is added; the precipitated magnesium hydroxide suspension is treated mechanically in four Dorr thickeners, each 200 feet in diameter. The thickened sludge is pumped to a filter tank into which Moore filter leaves are lowered; by means of suction a filter cake of moist magnesium hydroxide is formed on the leaves. The leaves are lifted by a crane to an adjoining compartment where the cake is blown loose and moved by a bottom screw conveyor to the neutralizing tanks, where 10 per cent hydrochloric acid dissolves it to form the chloride. The solution is concentrated in direct-fired evaporators to a stronger solution which is filtered, and then fed to a huge shelf drier (50 feet in diameter and over 50 feet high) not unlike a Herreshoff furnace. The still somewhat anhydrous product is mixed with flakes of some of the previously dried product and passed through a gas-fired rotary drier, where the drying is completed. The anhydrous product is now ready for the cells. The electrolyte overflow from the four Dorr thickeners is discharged into a canal which takes it seven miles away from the plant intake, so that it cannot dilute the incoming sea water. The chlorine from the cells is burned in natural gas and in hydrogen from other electrolytic processes (caustic) to form hydrogen chloride which after absorption in water is the acid used in the neutralizing tanks. A good part of the chlorine is thus recycled and

¹² U. S. Patent 1,851,817.

es over and over. The cells at Freeport are rather large, 6 feet by 12 in area, and produce about 1000 pounds of metal a day.

There is still another method for making magnesium chloride which consists of chlorinating a mixture of magnesite ($MgCO_3$) or magnesia (MgO) and coke in an electric resistance furnace in the shape of a tower. One electrode extends downward through the roof and reaches a bed of crushed coke in the lower part of which the other electrode is buried. The charge is fed in through suitable openings in the roof through which the gases may pass out. The chlorine is fed in at a point just above the bed of coke. The fused magnesium chloride travels through the bed of coke to an outlet at the very bottom of the tower. The product is anhydrous, and ready without further processing for the electrolytic cell; this is a great advantage, for the removal of the last portions of moisture from a magnesium chloride originally hydrous easily leads to decomposition and evolution of chlorine. The temperature in the chlorinating tower is $700-900^\circ C.$ ($12-1652^\circ F.$). There are modifications of this process which permit the use of dolomite.

The construction of electrolytic cells may be different in the various processes, although all decompose magnesium chloride into its elements. The Hulín type furnace, for example, is reported to be circular, to have a circular anode lining the sides, and central cathodes over which a removable cover is provided for the removal of the metal. The chlorine leaves by suitable connections near the anode.

Magnesium oxide which is obtained by calcining magnesia, or brucite ($MgO \cdot H_2O$), may be electrolyzed in a cell bath consisting of the fluorides of magnesium, sodium and barium; the latter raises the density markedly, helping the liberated metal to rise rapidly and preventing the suspended magnesium oxide from sinking too fast. The cell bath temperature is about $950^\circ C.$ ($1742^\circ F.$). Unlike aluminum oxide in cryolite, magnesium oxide dissolves only to the slightest extent in the molten fluoride electrolyte bath. There is no by-product in this cell process.

TABLE 35.—Relative weight of structural metals.

	Specific gravity	Relative weight	Weight per volume
Magnesium alloys	1.8	1.0	112 lbs./cu. ft.
Aluminum alloys	2.8	1.6	175
Zinc	7.1	3.9	443
Cast iron	7.2	4.0	450
Steel	7.9	4.4	493
Copper	8.9	4.9	556
Lead	11.3	6.3	706

The electrolytic methods just described furnish the world with essentially all of its magnesium metal. The direct electrothermal reduction process in which magnesium oxide is reduced to metal by carbon presents difficulties of operation.* The principle is as follows: a mixture of magnesia (MgO) and coke is heated to $1900^\circ C.$ ($3452^\circ F.$) in an electric furnace, at which temperature magnesium metal and carbon monoxide form. Unless the

*February 11, 1942. Plants said to be operating by this process or modifications of it are three; one at Konan, Korea; Swansea, Wales; Santa Clara, California.

mixed vapors are cooled rapidly, to 200° C. (392° F.), for example, the reversion: $\text{MgO} + \text{C} \rightleftharpoons \text{Mg} + \text{CO}$, with the re-formation of the original raw material. The cooling is achieved by a stream of cold hydrogen or natural gas which is mixed with the vapors; oxygen must be avoided. The magnesium metal is collected in a cooling drum, the finer particles in an electrical precipitator and a bag filter which follows it. The crude metal is 60-65 per cent Mg, and must be redistilled in an atmosphere of hydrogen in electrically heated retorts. At the plant built at Santa Clara, Calif., a ton of magnesium was expected to be furnished by each of the 36 retorts every third day, but the process, known as the Hansgirg, or Radent process, may be abandoned there because of difficulty in preventing explosions.

Pidgeon Process. Eminently suited for war-time production is the Pidgeon process,[†] in which ferrosilicon and magnesium oxide or dead-burned dolomite are made into briquets and heated in closed, evacuated, alloy-retorts. The temperature is 1150° C. (2102° F.). Magnesium metal collects in the condenser attached to the retort in solid masses, precluding possibility of explosion. Each pound of silicon produces theoretically 10 pounds of magnesium; each pound of 75 per cent ferrosilicon produces 1 pound of magnesium. This safe process requires only simple apparatus; the installation is rapid (3 months for complete plant), the cost low. In peace time, the ferrosilicon method will probably be superseded by the electrolytic one.

Magnesium is used both as such and in the form of alloys. The pure magnesium base alloys with 85 per cent and more magnesium serve for many fabricated products (65 per cent). Aluminum alloys and other alloys consume about 30 per cent of the magnesium production. The aircraft industry uses 80 per cent of the structural magnesium alloy products, mainly in the construction of engines. Magnesium alloys can be cast, rolled, forged, and machined.

TABLE 36.—*Typical properties of cast and wrought magnesium alloys.*

Alloy Designation	Nominal Composition* (%)			Tensile Strength	Yield Strength	Elongation (%)
	Aluminum	Zinc	Manganese	(lbs. per sq. in.)		
AM265 as cast	6	3	0.2	27,000	11,000	6
AM265-T4 Cast and Heat- treated	6	3	0.2	37,000	12,000	9
AM260-T6 Cast and Heat- treated	9	2	0.2	38,000	20,000	3
AM3S Sheet (annealed)....	1.5	32,000	17,000	10
AM-C58S Forging	8.5	0.5	0.2	45,000	30,000	65

* Balance magnesium.

Magnesium serves also for flares and incendiary explosives; for flushing radio tubes to remove traces of gases which pumps and charcoal can remove.

[†] "Magnesium from dolomite by ferrosilicon reduction," by D. H. Killeffer, *Chemical and Engineering News*, 20, 369 (1942).

Magnesium salts have been produced from various sources, from bitters, brines, and from sea water directly.*

For the production of one pound of

aluminum	there are required	10 kilowatt hours
magnesium	there are required	9-10 kilowatt hours
sodium	there are required	7 kilowatt hours

The production of magnesium during 1940 in the United States was 0 tons, twice what it had been in 1939 or 1938, and twenty times the production in 1929. The 1941 production is expected to be 15,000 tons, and 1942 production must be over 25,000 tons to provide enough metal for military requirements of the country. The world production in 1940 44,000 tons. The price during 1940 was 27 cents a pound.

SODIUM

Sodium metal was made originally by the electrolysis of fused caustic soda the metal as the sole product. Cells holding 250 pounds of melted caustic with a central iron rod as cathode, surrounded by a nickel perforated cylinder as anode, were operated within the range of 315° to 320° C. (599° to 608° F.). The current efficiency was 45 to 55 per cent, the voltage 4.5 to 5.5 volts per cell. The total reaction in the cell may be written: $4\text{NaOH} \rightarrow 4\text{Na}(\text{cathode}) + 2\text{H}_2\text{O} + \text{O}_2(\text{anode})$.

The present method for the manufacture of sodium metal is the electrolysis of purified and absolutely dry fused salt NaCl. Sodium made electrolytically from salt is much cheaper than that made from caustic, since the latter is itself a manufactured article, whereas salt is found in nature. Besides, a second product, chlorine, is obtained in a high state of purity. Downs cell¹³ operates on fused salt. The operation is continuous; the sodium produced is collected in a separate compartment, and withdrawn from there periodically. The chlorine is sent out free from moisture, and is collected in gas form, or as a liquid (see page 105).

At the carbon anode, 1, the chlorine gas is evolved, and is collected in a dome 3; it passes out under its own pressure. The cathode, 2, is an annular iron or copper piece, which surrounds the circular anode. The cathode is hooded by two metal screens. Sodium metal is generated at the cathode and is collected in the sodium collector marked 4, just above the cathode. The melted sodium is lighter than the fused salt, and rises readily. The collector is provided with a riser, 5, which delivers the sodium to a closed compartment, from which it is withdrawn at stated intervals. The level of fused salt in the bath is kept high enough to force the column of sodium along the delivery arm in the riser. Fresh salt is introduced at 7, and as it fuses it loses any water it may contain, which passes out to the atmosphere.

Sodium chloride fuses at 800° C. (1472° F.), but the cell is operated at a lower temperature, such as 600° C. (1112° F.), thanks to the addition of

* *Occurrence of raw materials for magnesium compounds*, by Paul V. Manning, *Chem. Met. Eng.*, 43, 936.

* *Sodium metal and compounds*, by Paul D. V. Manning, *Chem. Met. Eng.*, 45, 478 (1938).

* *Magnesium compounds from ocean water*, by H. Henry Chesny, *Ind. Eng. Chem.*, 28, 383 (1936).

U. S. Patent 1,501,756 (1924), to J. C. Downs.

materials to the bath which do not suffer decomposition. This lower temperature avoids the sodium metal fog which baffled all efforts to collect the metal produced. Furthermore, at such lower temperature, the cell has a longer life, and the chlorine is handled more easily. A certain amount of hydride of sodium (a white solid) forms, and gives rise to small explosions. The current efficiency is high, above 80 per cent, and the cells are as large as "20,000 ampere units." The decomposition voltage for fused NaCl at 600°C. is 3.59; operating voltage, 7 to 8. The Downs cell is an American invention, and its worth was proved in American plants; since 1929, it has been used in Germany.

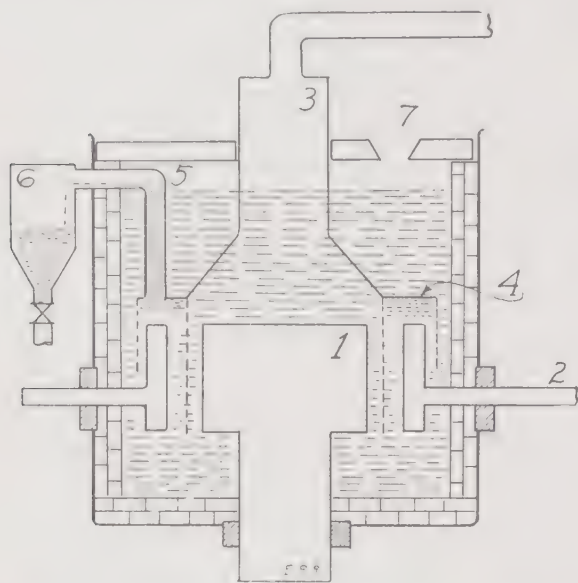


FIGURE 111.—The Downs cell, producing metallic sodium from salt. 1, carbon anode; 2, iron cathode; 3, dome for escaping chlorine; 4, annular sodium collector.

An electrolytic cell-furnace for sodium, which is reported in successful operation in Germany, has a long, knife-like iron cathode running longitudinally in the center of the cell, with an internal slit-like passage for the upward trip of the sodium metal, and an inclined cover piece, also part of the cathode, to deliver the molten metal to an outer receptacle.¹⁴

Sodium sells at about 20 cents a pound. It is a soft solid, and is shipped in the form of 12-pound bricks, packed in air-tight drums. Sodium is an industrial chemical; it is the raw material for sodium peroxide, sodium cyanide, and is the basis of the lead alloy used in manufacturing tetraethyl lead; it may be used to improve the structure of various alloys, to purify molten metals, in organic manufacturing condensations and reductions. It may be made into a chlorine-free sodium hydroxide, by adding the metal, with suitable precautions, to a concentrated hydrous caustic solution. The properties listed in Table 37 may lead to other applications.¹⁵

Sodium Peroxide. Sodium peroxide, Na_2O_2 , a white powder, is made in two stages. First, the metal is placed in a revolving steel drum with dehydrated air passing over it; sodium oxide, Na_2O , is formed. This white

¹⁴ U. S. Patent 1,820,844; of interest also 1,074,988 and 1,092,178.

¹⁵ Sodium has been used as a liquid partly filling the hollow stem of the valve in an airplane motor in order to dissipate heat which otherwise would have no escape.

TABLE 37.—Physical properties of various fluids suitable for transmission of heat including metallic sodium.

Property	Sodium	Mercury	Tin	Meprolene Oil	Diphenyl (C ₆ H ₅) ₂	Water
Melting point, °C....	97.5	-38.8	232	0±	69	0
Boiling point, °C....	883° C.	357	2270	300±	255	100
Specific gravity, mm.	677° C.					
Specific gravity, mm.	565° C.					
Specific gravity, gms./cc.	0.834 (98-883° C.)	12.9 (100-400°)	6.93 (232-400°)	0.91 (20°)	.85 (255°)	0.998 (20°)
Specific heat, lbs./gal.	6.9	107	57.5	7.6	8.7	8.3
Specific heat, cal./gm.33 (100° C.)	.033 (20°)	.058 (250°)	0.5±	.559 (300°)	1.0
Thermal conductivity	0.21	0.02	0.15	0.004	0.0013
Thermal conductivity coefficient..	0.01 (200-300°)	0.01± (250°)	1.0±	0.010 (20°)
Heat of vaporization, /gm.	1100	65	621	74.4	539

der is transferred to a second revolving drum set in brick work so that may be applied; dry oxygen is passed into the heated drum, until no is absorbed. The product now is the peroxide, Na₂O₂. It is valuable oxidizing agent for a number of minor chemical operations; it serves to make hydrogen peroxide, metallic peroxides, perborates, and other "per" compounds. It has gained in importance of late years because it is used in the manufacture of benzoyl peroxide, called "Lucidol,"¹⁶ the bleaching agent for white flour. The benzoyl peroxide is made from benzoyl chloride and sodium peroxide; it is a white powder, 2C₆H₅.CO.Cl + Na₂O₂ = 2C₆H₅.CO.O.O.CC₆H₅ + 2NaCl. For use in the flour mills, the benzoyl peroxide is diluted with calcium phosphate, and is then called "Kadelox."¹⁷ The application is by running in a small stream of "No-lox" into the regular stream of flour from the spout, as delivered to bins; there is no other mixing. After a day, the bleaching agent has done its work. It is used in such small amounts that no trace of it can be detected by chemical means.

Sodamide. Sodamide, NaNH₂, a solid, is made by the action of dry ammonia on metallic sodium; it is important in the synthesis of indigo.¹⁸ Heated with carbon to 800° C. (1472° F.), sodamide is changed¹⁹ to *sodium cyanide*, NaCN,



which is run off as a liquid from the furnace and may be cast into convenient shapes (cyanide egg). It is customary to combine the two steps in making cyanide, and to place sodium metal and carbon as charcoal in the covered reaction pots (iron) and pass in the ammonia gas. Heat is applied from the outside; the hydrogen is allowed to burn on reaching air, or is sent to a gas-holder for re-use in making direct synthetic ammonia.

U. S. Patent 1,380,334.

U. S. Patent 1,381,079.

Chapter 28.

German Patent 148,045

POTASSIUM PERMANGANATE

The step in the manufacture of permanganate which may be performed in an electrolytic cell is the change of potassium manganate, K_2MnO_4 , green in color, to potassium permanganate, $KMnO_4$, which is red; this change is an oxidation, which takes place at the anode. The liquor at the same time becomes alkaline, because of the formation of potassium hydroxide. A cell which has been found suitable for this oxidation is shown in Figure 112. The changes may be expressed in three reactions, which are summarized in the fourth:

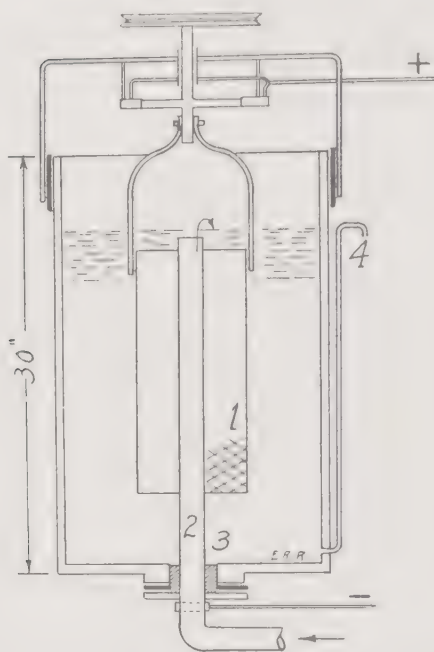
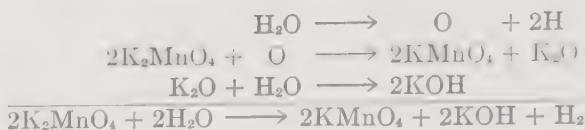
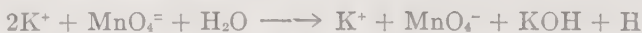


FIGURE 112. — Permanganate oxidation cell. 1, rotating wire-netting anode; 2, inlet pipe for liquor, also forming cathode; 3, sulfur insulation; 4, outlet for liquor.

This consideration has led to the term "anodic oxidation." Expressed in terms of ions, the manganate ion MnO_4^{2-} loses one electron at the anode, and becomes MnO_4^- , while at the same time one potassium ion K^+ is discharged at the cathode and becomes potassium metal, which reacts with water to form potassium hydroxide and hydrogen; two hydrogen atoms pass off to form one molecule of hydrogen gas:



The complete process of manufacture comprises a fusion of manganese dioxide, MnO_2 , with a caustic potash, KOH , in a muffle furnace with circulation of air, when the potassium manganate forms. The product of the furnace is leached, and the solution, after treatment to remove most of the excess caustic potash, is passed through the cell. The potassium permanganate is so insoluble that some of it separates in the cell; on concentrating another part is obtained.

Another procedure independent of current consists in passing carbon dioxide into the manganate solution, with the production of permanganate and hydrated manganese dioxide (artificial pyrolusite) as a by-product:



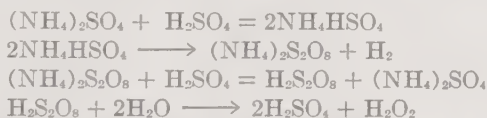
Potassium dichromate may also be made with the aid of the electrolytic cell. In general, however, it is made in the standard way. The ore (chromite) is crushed, powdered, and fused with alkali carbonate; the cooled mass is leached, and the chromate obtained. The dichromate is made by treating the chromate with mineral acid.

Chromic acid in red crystal form is made by treating the chromate or chromate with sulfuric acid of high concentration, and filtering through glass or wool felt.

Ammonium Persulfate. Ammonium persulfate, $(\text{NH}_4)_2\text{S}_2\text{O}_8$, a white, crystalline solid only slightly soluble in water, is made by the electrolysis of a water solution of ammonium sulfate containing sulfuric acid. The anode is a small platinum plate (hence high current density), the cathode a larger lead plate (hence low current density); the bath is kept cold by cooling coils in which brine circulates ($10^\circ\text{C}.$). The ammonium persulfate forms at the anode where it precipitates. This product is useful as an oxidizer for many minor purposes, and as a solvent for silver in photography.

Hydrogen Peroxide. Hydrogen peroxide, H_2O_2 , is sold in the wholesale trade in the form of a 30 per cent water solution. It is made by the electrolysis of persulfuric acid, obtained by the anodic oxidation of sulfuric acid at low, that is, room temperature. On heating the persulfuric acid solution under reduced pressure, the hydrolysis takes place, and a distillate consisting of hydrogen peroxide and water is obtained. The residual acid is used over again. The process is continuous.

Another way is by the intermediate formation of ammonium persulfate, with subsequent treatment with sulfuric acid to form persulfuric acid, which is then hydrolyzed by gentle heating; the hydrogen peroxide is distilled off at low pressure. The ammonium persulfate method has also been developed into a continuous process.²⁰ The residual liquor from the distillation is used over again, with addition of water. Theoretically at least, no water and current are consumed; in practice, a small amount of make-up material is required. The second product of the electrolytic oxidation, hydrogen, is generally wasted. The reactions are:



Besides the electrolytic methods, which account for the bulk of the production, hydrogen peroxide may also be made by chemical methods, of which two will be described. The barium peroxide method retains some importance only because it has a salable by-product, blanc fixe. Barium peroxide is heated to $600^\circ\text{C}.$ ($1112^\circ\text{F}.$), and dry air is passed over it; the

²⁰ U. S. Patent 1,234,380.

barium peroxide, BaO_2 , which forms, is cooled, and then treated with a moderate amount of steam. The resulting suspension, essentially of formula $\text{BaO}_2 \cdot 8\text{H}_2\text{O}$, is fed into dilute sulfuric acid containing some phosphoric acid; hydrogen peroxide is liberated and barium sulfate (blanc fixe²¹) precipitates. The latter is filter-pressed, washed and sold wet to paper mill. The solution of hydrogen peroxide is adjusted to proper strength by distillation.

The second chemical method consists of treating sodium peroxide in solution with sulfuric acid. The sodium sulfate formed is soluble, and is removed from solution by adding sodium fluoride and cooling to -2°C (28.4°F). The supernatant solution of hydrogen peroxide still contains about 3 per cent of mineral matter, which however does not generally interfere with its applications.

The 30 per cent hydrogen peroxide is also labeled "100 volumes," because one volume liberates 100 volumes of oxygen under standard specific conditions; similarly the 3 per cent solution, the accepted pharmaceutical strength is "10 volumes." The 30 per cent commercial grade by the electrolytic method is exceedingly pure; it is stable in the absence of all suspended solids. A trace of stabilizing substances is sometimes added. The pharmaceutical grade contains a small percentage of acetanilide to reduce the tendency of oxygen to split off during storage; its value as a disinfectant is due to the quick liberation of oxygen when exposed to air.

Hydrogen peroxide serves in the industries to make metallic peroxide, such as calcium peroxide, and also to make sodium perborate. It is a bleaching agent, favored in the textile, felt hat, and other industries because it leaves nothing but water after it has functioned. It is used in the preparation of certain breads and cakes, and as a disinfectant. Hydrogen peroxide is being manufactured at the rate of many tons a day. In 1939 the U. S. production was 21,487,968 pounds* of hydrogen peroxide 30 per cent H_2O_2 valued at 15.6 cents a pound; other peroxides produced had a value of \$936,824. The 30 per cent hydrogen peroxide is shipped in glass carboys, aluminum drums or aluminum car tanks.

OTHER PATENTS

U. S. Patent 1,839,756, on an apparatus (cell) for electrolyzing fused NaCl , and 1,826,773, on the method of salt feed; on the collection of magnesium in the electrolytic cell. German Patents 344,427 and 302,024; on the electrolysis of NaOH for sodium. German Patents 344,427 and 302,024; U. S. Patent 1,875,760, electrolysis of molten magnesium chloride; 1,820,022, production of metallic magnesium by electrolysis of fused MgCl_2 ; 1,878,939, metallic aluminum by thermal reduction of oxide ores; 1,833,806, electrolytic refining of aluminum; 1,770,940, chemically pure aluminum by electrolysis; 2,021,385, removal of acid from peroxide solutions, to Joseph Reichert; 2,008,726, storing and handling hydrogen peroxide solution; 2,004,809, 2,022,860, on stabilizing hydrogen peroxide; 2,017,410, on hydrogen peroxide purification; 2,022,650, on hydrogen peroxide process; 2,051,303, on the reaction of sodium with hydrocarbons, to Norman D. Sear; 2,065,744, on the production of sodium perborate; U. S. Patent 1,921,377, the Warrington magnesium and chlorine cell.

PROBLEMS

1. An aluminum furnace is to produce 120 pounds of metal per day. How much alumina will be required, if the yield is perfect, and how much carbon will be consumed at the anode if reaction (2) given in the text takes place exclusively?

²¹ Chapter 31.

* Bureau of the Census.

Sea water contains 0.48 per cent MgCl_2 . In order to produce one ton of magnesium, how many gallons of sea water must be treated with lime to produce magnesium hydroxide, and how much lime and how much hydroxide will be involved? How much chloride will be formed from the hydroxide, ready for the cell? The current in each case may be assumed to be 100 per cent.

A bank of 20 cells produces 6 tons of sodium per day. The feed is purified sodium chloride, and is steady throughout the day. How much NaCl per hour must be fed into the 20 cells and how many pounds of chlorine will be collected? Let the sodium recovery be perfect, and the chlorine recovery be 92 per cent.

The decomposition voltage in the electrolytic cell is found by means of the equation $E = Q \times 4.1834 \div [96580 \times n]$, in which E is in volts; n is the number of equivalents involved; Q is the heat of formation of all the substances taking part in the reaction, the heat for the substances on the left being taken as positive, and the heat for those on the right are taken as negative. This first value of Q must be corrected for the heat already present in the fused substances in the electrolytic cell. The mole heat (which is the product of specific heat and molecular weight) is subtracted for each substance on the left of the reaction (here a single substance) is subtracted from the Q value, also in calories, originally found; the reduced value serves to compute E . Apply to fused salt NaCl , at 600°C . cell bath temperature.

Heat of formation of solid NaCl , 58.46 grams	97.700 gr. cal.
Heat of fusion, at the melting point, 804°C	7200 gr. cal.
Heat of the melt at 600°C . = 585×13.33	7798
	<hr/>
	- 14,818
	<hr/>
	82,882

$$[2 \times 4.1834] \div [96.580 \times 1] = 3.59 \text{ volts} = E$$

The decomposition voltage of sodium chloride fused at 600°C . is 3.59 volts.

The heat of formation at 15°C . of MgCl_2 is 151,000 calories. Its mole heat is 26,200 calories. The electrolytic decomposition is performed at 700°C . The heat of fusion is 7,000 cal. (est.). What is the decomposition voltage, remembering that $n = 2$? Compare with the figure in the text.

The heat of formation of Al_2O_3 is 378,000 calories. The heat of formation of Al is 26,200 calories. The heat of fusion of alumina is 5188 calories for the mole. If electrolysis takes place at 915°C ., and the mole heat of alumina is 20.4, what is the decomposition voltage for the reaction $\text{Al}_2\text{O}_3 + 3\text{C} = 2\text{Al} + 3\text{CO}$? What is the decomposition voltage if the reaction is $\text{Al}_2\text{O}_3 + 1\frac{1}{2}\text{C} = 2\text{Al} + 1\frac{1}{2}\text{CO}_2$? The heat of formation of CO_2 is 94,200 calories. Answer: For the first reaction, 1.99 v.; for the second, 1.54 v. What are the theoretical weights of the metals deposited per faraday (96,580 coulombs) for the metals in problems 4, 5 and 6, and what are the weights of the metal salts decomposed by one faraday? What are the actual weights of these salts decomposed, taking into account the current efficiency stated in the text?

Heat of formation of MgCl_2	151,000 calories
Heat of the bath, if all MgCl_2	$18.5 \times 685 = 12,672$
Heat of fusion of MgCl_2 (est.)	7,000
	<hr/>
	19,672
	<hr/>
	141,328

$$[141,328 \times 4.1834] \div [2 \times 96,580] = 3.05 \text{ volts.}$$

Problem for problem 6

First reaction $\text{Al}_2\text{O}_3 + 3\text{C} = 2\text{Al} + 3\text{CO}$ at 915°C	378,000 calories
Heat of formation of alumina	
Heat of formation of 3CO	$3 \times 26,200 = 78,600$
Heat of the alumina in cell bath	$20.4 \times 900 = 18,360$
Heat of fusion	$50.9 \times 101.94 = 5,188$
	<hr/>
	102,148
	<hr/>
	275,852

$$[275,852 \times 4.1834] \div [6 \times 96,580] = 1.99 \text{ volts.}$$

Second reaction $\text{Al}_2\text{O}_3 + 1\frac{1}{2}\text{C} = 2\text{Al} + 1\frac{1}{2}\text{CO}_2$

Heat of formation of alumina		378,000 cal.
Heat of formation of $1\frac{1}{2}\text{CO}_2$	141,300	
Heat of alumina in cell bath	18,360	
Heat of fusion	5,188	
	<hr/> 164,848	<hr/> 164,848
		<hr/> 213,152

$$[213,152 \times 4.1834] \div [6 \times 96,580] = 1.55 \text{ volts.}$$

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The utilization of gases on the industrial scale is one of the triumphs of modern chemical engineering; the seamless steel cylinders in which some of them are transported, under pressure, are familiar sights on trucks and rail-cars. Gases serve as chemical agents, refrigerants, anesthetics, disinfectants; they also serve in beverages, for flames, and to stifle flames.

Chapter 19

Industrial Gases

The gases included in this chapter fall into two groups: hydrogen, H_2 , helium, He, oxygen, O_2 , nitrogen, N_2 , and argon, Ar, the less easily compressible gases; and chlorine, Cl_2 , sulfur dioxide, SO_2 , ammonia, NH_3 , carbon dioxide, N_2O , carbon dioxide, CO_2 , carbon monoxide, CO, acetylene, C_2H_2 , and ethyl chloride, C_2H_5Cl , the more easily compressible gases. At ordinary temperatures, the former do not liquefy in spite of considerable pressure; the latter at ordinary temperatures form liquids under rather moderate pressures; hence the content by weight of a standard cylinder for the gases in the first group will be small, for those in the second group, considerable. It follows that gases in the first group will be used as free gases at once upon generation, or will be shipped short distances, from many small plants, each serving small territories; whereas gases in the latter group will be economically shipped long distances, from a few central plants.

In addition to a variety of technical uses, several members of the second group serve as ordinary refrigerants—ammonia, carbon dioxide, sulfur dioxide, and ethyl chloride: to these must be added the newer refrigerants, chloro-difluoromethane, propane, and butane, which are discussed in Chapter 12. Members of the first group are used as extraordinary refrigerants; for example, nitrogen in liquefaction of the carbon monoxide impurities in hydrogen.

HYDROGEN

Of late years, hydrogen has become of industrial importance in the direct synthesis of ammonia, in the hydrogenation of fatty oils, of petroleum oil fractions, of coal, of hydrocarbons, and single organic substances; its other uses are for balloons and dirigibles, and for hydrogen-air, hydrogen-oxygen, atomic hydrogen flames.

It is obtained from water gas, producer gas, or coke-oven gas, by the removal of the non-hydrogen constituents; it is made by the action of steam on oil refinery gases and natural gas, by the thermal decomposition of natural gas, by steam on heated iron, by the electrolysis of water, and by miscellaneous processes. It is a by-product in the electrolytic cell for caustic soda in several fermentation processes, and in others. The choice of a process must be decided by the resources at hand, and by the degree of purity required. Rapid generation with a minimum of apparatus in an isolated plant may be demanded; in such a case the ferrosilicon process would serve. **The Water Gas and Steam Process, a Continuous Catalytic Process.** Water gas¹ with steam in excess is passed over an iron oxide catalyst, just

as is done in the Bosch process described in Chapter 6, except that since producer gas is added, the amount of nitrogen is small. The converter has several trays, on which the catalyst rests. The reaction



is exothermic; as the temperature must be maintained at 450° C. (842° F.) the converters are insulated and the incoming gases heated in exchange. Once the reaction has begun, no outside fuel is required. Three volumes steam to one of gas are used; the great excess of steam drives the reaction to the right. After passing the exchangers the reacted gas is freed from steam by water-cooling. The carbon dioxide formed, as well as the small amount which entered with the water gas (4 per cent), is removed by scrubbing with cold water while under pressures of 25 to 30 atmospheres, in steel towers; under such pressures carbon dioxide is freely soluble in water. The gas leaving the last scrubber has the composition:

	Per cent
Hydrogen	92-94
Nitrogen	1-4
Methane	0.5
Carbon monoxide	2-4
Carbon dioxide	small
Moisture	small

The crude hydrogen may be further purified from carbon monoxide by scrubbing in ammoniacal cuprous chloride solution. The nitrogen impurity may be lowered by careful operation of the water-gas plant. The methane is not wanted, and may be almost avoided by using well-burned coke.

A similar process in which the catalytic agent is lime at the temperature of 450° C. (842° F.) instead of iron oxide has been proposed; its great advantage is that the carbon dioxide is simultaneously removed. Unfortunately this absorption is accompanied by a powdering of the lime granules, as the carbonate forms, and the powder tends to clog the lime tower.

Water Gas Process with Liquefaction of the Carbon Monoxide. There are two processes in which the carbon monoxide is liquefied by cold and pressure and removed in that state, leaving the hydrogen gas comparatively pure. The Linde-Frank-Caro process uses liquid air boiling under a few millimeters of pressure for the final cooling of the water gas already pre-cooled by three steps, first by an ammonia refrigerating system (-35° or -31° F.), then in an exchanger wherein the uncondensed hydrogen takes up heat, third by the liquid carbon monoxide separated in the final cooling. The carbon monoxide at the same time boils, and is used as a gaseous fuel. The other process is Claude's, who uses no liquid air, but obtains the necessary final cooling by the expansion of hydrogen from a pressure of 20 atmospheres to a lower pressure while doing work against a piston. The hydrogen is pre-cooled in exchangers by outgoing gases, and by the evaporation of the carbon monoxide which has been previously liquefied.

The hydrogen in coke-oven gas,² and in the gas from petroleum-crack stills may be recovered by liquefaction of the non-hydrogen components.

² Chapter 6; and *Ind. Eng. Chem.*, 14, 1118 (1922).

Steam on Heated Iron. Many units based on the reduction of steam by iron at an elevated temperature are in use, chiefly in connection with the hydrogenation of fatty oils. The hydrogen obtained by this process is purer than by the continuous catalytic process; the latter can be purified, but the iron and iron process has the further advantage that it is suited to small-sized installations, such as are usually required for the hydrogenation of oils. The reaction is



The oxide formed, when running from left to right, must be reduced at short intervals; this is best done by water gas, preferably purified. The iron should have a porous structure and little tendency to disintegrate; a red carbonate (spathe ore) has been found suitable. The iron is placed in eight steel retorts, 9 inches in diameter and 12 feet high, grouped in sets of 12 retorts each. The steaming period (hydrogen production) is 10 minutes, the steam traveling upward; the water-gas period lasts 10 minutes, because the reduction of the oxide is slower than its oxidation; water gas travels downward. A brief purging with steam sends the first hydrogen to the water-gas holder.

By means of such an arrangement a continuous flow of hydrogen is obtained; with the retorts given above, a volume of 3500 cubic feet, about 100 cubic meters, is obtained per hour. The spent water gas is cooled in a scrubber, and burned (for it still contains combustible gases) around the retorts to maintain the reaction temperature, 650° C. (1202° F.). The steaming reaction is exothermic; the water-gas reaction is endothermic (cooling).

The hydrogen passes out with the great excess of steam employed in order to drive the reaction to the right. It is cooled in scrubbing towers, freed from carbon dioxide and hydrogen sulfide by lime purifiers. The hydrogen obtained is 98.5 to 99 per cent pure; by careful purging, using closed purifiers instead of scrubbing towers, and other modifications, the purity may be raised to 99.94 per cent. The iron mass lasts six months, the retorts a year. There are many modifications of this process.

The hydrogenation of an oil is retarded appreciably by a carbon monoxide content of even 0.25 per cent; the custom is to produce the hydrogen to as great a purity as careful operation permits, and beyond removing hydrogen sulfide and carbon dioxide, to make no purification.

In the continuous catalytic process 1.25 volumes of water gas are required for 1 volume of hydrogen (on the basis of 100 per cent hydrogen). In the water-gas method, which involves removal of carbon monoxide by oxidizing it, 2.5 volumes of water gas are required for 1 volume of hydrogen, mainly as fuel for machinery. In the reduction of water by hot iron, water gas is used to revivify the iron, and the amount is 2.5 volumes for one volume of hydrogen produced. The continuous catalytic process has therefore a marked advantage over the other two processes.

Electrolysis of Water. In commercial cells, direct current is passed between iron electrodes, which may be nickel-plated, in a 10 to 25 per cent caustic soda solution. The caustic soda is not consumed; only water needs

to be added as the electrolysis proceeds. The hydrogen is generated at the electrode (cathode), the oxygen at the other (anode). Cells differ in method of gathering the two gases, in other details of construction, and size. The efficiency varies also, but not very much; an average figure will be 7.5 cubic feet of hydrogen per kilowatt hour, and 3.8 cubic feet of oxygen at the same time. Assuming that the oxygen is wasted, and that the cells are run for the production of hydrogen only, the cost of current will determine the cost of the gas. If the horsepower year is \$20, a low figure, 1000 cubic feet of hydrogen will require 40 cents for power. With higher prices for horsepower, the cost for power per 1000 cubic feet will be correspondingly greater. The continuous catalytic process produces 1000 cubic feet of hydrogen for about 45 cents, granted favorable conditions for coke and coal. If both hydrogen and oxygen are required, electrolytic cells are the proper devices.

The decomposition voltage for the reaction $\text{H}_2\text{O} = \text{H}_2 + \frac{1}{2}\text{O}_2$ is 1.23; the operating voltage about 2. The amperage varies with the size and intensity of operation; with maximum load, it may be as much as 10 amperes for electrodes 40 inches wide by 60 inches high. The electrodes are separated by an asbestos diaphragm, and suspended in cast-iron containers.

One of the large-scale installations³ for the electrolytic production of hydrogen consists of 306 cells, each with 20 plates. The electrolyte is 99 per cent very pure potassium hydroxide, maintained at 60° C. (140° F.) by the Knowles patented regulator. Each electrode receives 500 amperes, hence 10,000 amperes per cell. The production is 49,000 cubic feet of hydrogen per hour, 99.5 per cent pure, and half that quantity of oxygen. The cells are fed with distilled water. This gas is used in making synthetic ammonia, as part of large auxiliary plants for the manufacture of chemical fertilizer.

Cells operating under pressure and delivering gas at 200 atmospheres have been proposed; the energy required for electrolysis decreases as the pressure is increased.⁴

Other Processes and By-product Hydrogen. Hydrogen gas is prepared by the thermal decomposition⁵ of natural gas, particularly in California where the state law prohibits the wasting of natural gas. The operation is a cracking of the gas, and is performed in apparatus similar to those used for making water gas. A five-minute cycle is used: the gas is burned to heat up the checkerwork in the generator (2 min.); then the gas, with air, is passed in. Elemental hydrogen gas with suspended carbon particles forms; the carbon is filtered out in bag filters. After 2 minutes, the generator is too cool, and the cycle is repeated.

In the oil industry, hydrogen may be prepared from hydrocarbons in the refinery gases, or in available natural gas, by treating with steam, with or without a catalyst. The reaction is $\text{CH}_4 + 2\text{H}_2\text{O} = 4\text{H}_2 + \text{CO}_2$.⁶ For

³ Knowles Hydrogen plant at Warfield Works, Consolidated Mining and Smelting Co., Ltd., Canada. *J. Soc. Chem. Ind.*, **51**, 355 (1932). An interesting cell for the electrolysis of water is that of the National Corporation, Ltd., Toronto.)

⁴ *Trans. Inst. Chem. Eng. (Brit.)*, **9**, 154 (1931).

⁵ *Chem. Met. Eng.*, **39**, 381 (1932).

⁶ *Ind. Eng. Chem.*, **22**, 1030 (1930).

reaction $\text{CH}_4 + \text{H}_2\text{O} \rightarrow \text{CO} + \text{H}_2$, the catalyst nickel-magnesia, and temperature 800°C. are suitable.

The by-product hydrogen from the electrolytic caustic cell is discussed in Chapter 5; from fermentation⁷ in Chapter 20; and its utilization in Chapter 25.

In the ferrosilicon process, powdered ferrosilicon containing as much iron as possible (90 per cent is frequent) is added to a 20 per cent solution of caustic soda at a temperature of 80° to 90°C. ; very pure hydrogen is needed. Aluminum in the form of shavings also gives hydrogen with a solution of caustic soda. An alloy of sodium and lead reacts with water to give hydrogen, again of high purity (hydronex). These three processes are used for military purposes and as supplementary plants for emergency or temporary operations.

Helium. This comparatively rare gas is produced in large quantities at Amarillo, Texas; it occurs in a number of natural gases in amounts varying from 0.5 to 7 per cent, averaging near 3 per cent. The gas is compressed, cooled, and the non-helium portion removed by liquefaction; 97 per cent He with some nitrogen is obtained.⁸

Helium is used for dirigibles; its value lies in the fact that it forms no explosive mixture with air. The Macon was a helium ship; it was wrecked on the California coast because of a structural defect. Just before that the USS Shenandoah, also a helium ship, was destroyed in a storm over the Atlantic, not far from Barnegat Bay in New Jersey. There is left to the United States only the Los Angeles. The catastrophe to the hydrogen-filled Hindenburg (May, 1937) will lead to the use of helium for the German ships. The lifting power of helium is 92 per cent of that of hydrogen.

A portable helium repurification plant has been designed.⁹ It is estimated that the helium reserves already in sight are 10 billion cubic feet, in the United States alone. There is a potential production of 200,000 cubic feet per day from the gas in the boric acid fumaroles in Italy. Canada has a low percentage helium material.

OXYGEN¹⁰

The great importance of industrial oxygen is due to the usefulness of the oxyacetylene torch for steel welding and steel cutting, and to a lesser extent to the oxyhydrogen flame. The possibility of an extension of its use lies in the increased temperature given by gas when burned in oxygen instead of in air. In the blast furnace for iron wherein the amount of useless, heat-consuming nitrogen may be reduced with a saving of coke and an increase in output. Liquid oxygen mixed with powdered charcoal may yet become an important and cheap explosive.^{10a}

⁸ *Ind. Eng. Chem.*, **18**, 1045 (1926).

⁹ "The production and uses of helium gas," by R. R. Bottoms, *Aeronautical Eng.*, **1929**, 197; also *Ind. Eng. Chem.*, **11**, 152 (1919).

¹⁰ *Ind. Eng. Chem.*, **22**, 1191 (1930).

^{10a} Based in large part on "Der Sauerstoff," by M. Laschén, published 1924 by Carl Marhold Verlagsgesellschaft, Halle a.S. Germany (100 pages); and on "Fluessige Luft," by Ludwig Kolbe, published by Johann A. Barth, Leipzig; the latter book contains several diagrams of complete plants.

^{10b} It is the regular explosive now for the iron mines in the East of France (Hayange).

The industrial method of preparation is the fractionation of mixture of liquefied air. Atmospheric air contains:

	Per cent by volume	Per cent by weight
Nitrogen	78.1	75.5
Oxygen	20.9	23.1
Argon94	1.29
Carbon dioxide03	.049
Water vapor	variable amounts	

The composition of liquid air varies slightly according to the conditions of liquefaction; on warming it, there passes out a gas containing 93 per cent nitrogen and 7 per cent oxygen, and there is left a liquid richer in oxygen than the original. Nitrogen boils at $-195.8^{\circ}\text{C}.$, air at -191° , oxygen at -183.0° , all under the pressure of 1 atmosphere. The difference in boiling points of nitrogen and oxygen is not quite $13^{\circ}\text{C}.$, the nitrogen being the more volatile. It is upon this fact that the fractionation is based.

In the liquefaction of air the following steps are included: *a*, the removal of carbon dioxide and dust; *b*, compression to high pressure; *c*, removal of moisture; *d*, cooling to low temperature in exchanger coils; *e*, liquefaction by expansion in the separator.

During the operation of the liquefying system three periods must be distinguished: the starting period, in which the apparatus is brought from room temperature to the low temperature essential for liquefaction (1 hour); the running period, during which the liquefaction proceeds continuously (1 week to 1 month); and the thawing-out period, during which the carbon dioxide and water, which in spite of all purification accumulate in the system, are thawed and blown out by a stream of warm air. The length of the running period depends upon the efficiency of the purifying apparatus and on the demand, for appreciable stores with which to meet unexpected demand cannot be accumulated in periods of low business activity. The liquefied air is fractionated in single or double columns, and the oxygen is compressed in the shipping cylinders.

The cooling during the running period is mainly due to the latent heat of evaporation of the liquefied air. In the starting period, the cooling is partly due to the expansion of the compressed air against atmospheric pressure, and partly to the Joule-Thomson effect.¹¹ To insure a considerable cooling during both cooling and running period, the Claude system expands a part of the compressed gas, after it has been precooled considerably against the piston of an engine driving a dynamo. In the performance of the considerable amount of work by the gas as such, a cooling of $75^{\circ}\text{C}.$ is secured. Several American plants operate under the Claude license. The description which follows will not include this feature, in order to avoid confusion.

The Liquefaction of the Air. The atmospheric air is drawn into a first stage compressor, with four separate cylinders, for plants producing 15 cubic meters¹² (530 cubic feet) of free oxygen¹³ per hour; for larger plants, for

¹¹ Cooling due to energy consumption in overcoming the attraction between molecules.

¹² 1 cubic meter = 35.31 cubic feet.

¹³ Free oxygen means oxygen measured under a pressure of one atmosphere.

compressors are preferred; three-stage compressors are used less than two. After each compression, the air enters a coil set in running cold water so that it enters the next stage at room temperature. The rise in temperature for the compression is approximately the same for each of the stages, to 170°C .

The carbon dioxide may be removed before reaching the compressor, by passing the air through two towers working in series, filled with coke, down which a solution of caustic soda or caustic potash travels; the air passes up the tower, on the countercurrent principle. The tower packing rests on the bottom; the liquor accumulates at the base and is circulated to the top of the tower by a small gear pump. Dust is caught at the same time. Another system is to remove the carbon dioxide in the compressed gas between the third and fourth stage.

Before entering the liquefying system, any water in the air must be removed, for water, like carbon dioxide, would deposit as a solid and plug small pipes or the expansion valves. The amount of water brought in with the air is considerable. In a plant making 15 cubic meters of oxygen per hour, taking in 120 cubic meters of air per hour containing 65 per cent relative maximum humidity at 20°C ., 193 kilograms¹⁴ of water enter in a day period. The greater part of that water is removed by liquefaction; the air from the several cylinders is cooled, and run off before the air enters the next stage; only that contained in the fourth-stage air, estimated at 48 kilograms, needs to be absorbed by a special device. This consists of a cylindrical vessel with false bottom filled with fused calcium chloride. The air travels upward; the liquefied calcium chloride travels down and may be drawn off at intervals. Caustic potash may be used instead, and in that case its liquor can serve in the carbon dioxide-removing towers.

The compression in the several stages is shown below, and at the same time the volume which at the pressures stated weighs 1 kilogram¹⁴:

Stages	1	2	3	4
pressure	4.1 atmospheres ¹⁵	14.5	50	200
volume	86 liters	23.35	6.93	1.94

The pressures apply to the starting period; in the running period they are stated in the table for the first three stages, but the fourth is about the same as the third. Advantage is taken of this fact to send in during the running period so-called low-pressure air (25 to 50 atmospheres) which liquefies easily at the temperature of the liquefier, which is very near 0°C .; in this way an important saving in power is made.

As a rule the liquefying vessel and the fractionating column are combined, thus avoiding a transference of the liquid. For plants producing less than 15 cubic feet of oxygen per hour, the gas from the fourth stage is precooled by an ammonia refrigerating system; when this is done the water is thereby removed, so that a calcium chloride tower is not needed, and at the same time the air enters the exchanger at a temperature of

¹⁴One kilogram is 2.2 pounds.

¹⁵One atmosphere is 14.70 pounds per square inch.

-30° C., thereby increasing the liquefying capacity of the system considerably.

With a single-column rectifier the wasted gas is 93 per cent nitrogen, 7 per cent oxygen; the yield 66 per cent. With a double-column rectifier

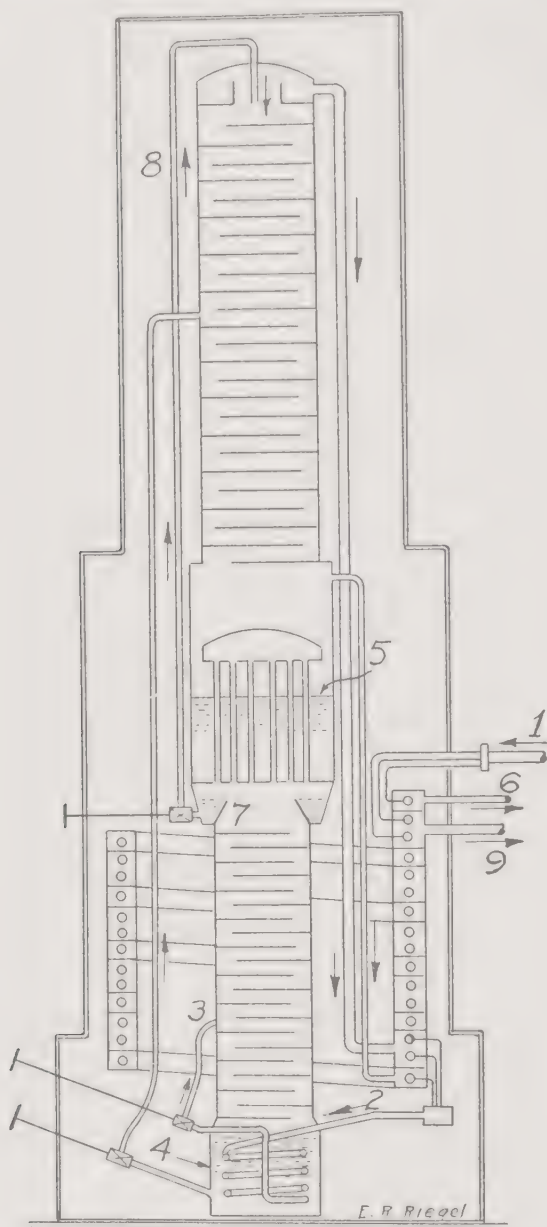


FIGURE 113.—Combined liquefier and separator with double column (Linde). The high-pressure air enters at 1, passes through exchanger coil 2, and is expanded reaching the lower column at 3; liquid rich in oxygen collects at 4, while the gas rich in nitrogen reaches the top of the column, is liquefied there and collects at 7; from here it passes through a valve into 8 and to the top of the upper column; the liquid rich in oxygen passes from 4 to the middle of the upper column, loses its nitrogen on the way down, so that oxygen collects at 5; the oxygen passes out here, traverses the exchanger and leaves by 6; the nitrogen gas leaves at top of still, passes the exchanger and leaves at 9. (Note: The curved dome over 7 causes the liquefied nitrogen to drip down through the outermost tube only, so that all of it reaches collector 7.)

the escaping gas has only 2 per cent oxygen, and the yield is 90 per cent. The latter is shown in Figure 113.

Two important principles are used; the interchange of heat in double coils, and the rectification of the liquid by means of the columns and shelves. Referring to Figure 113, of the liquefier combined with the double column rectifier, the entering air passes through the inner coils of a double

coil system, while the outgoing oxygen and nitrogen surround them. Entering air loses heat to the outgoing gases, and it will be noted from the drawing that the coldest oxygen meets the air already cooled in the air coils; the warm entering air, on the other hand, can still lose heat to oxygen (and nitrogen) which has passed through all the coils and is about to leave the system. The compressed air thus reaches the coil in the middle of the column well precooled; it cools still further in contact with the liquid in the column, and when it reaches the expansion valve, it liquefies completely. This accomplished, the two constituents are separated by permitting the liquid to drop from shelf to shelf, in contact with the rising gas. On each shelf, an interchange takes place; the liquid loses a part of its more volatile constituent, nitrogen, and robs the gas of a part of its less volatile constituent, oxygen, so that the liquid which reaches the lower shelf is richer in oxygen than the liquid on the shelf just above it. The separation is completed in the upper column, as indicated in the illustration.¹⁶ As the liquid from the lower column at 4 enters the shelves in the upper column, and ascends, it gains in oxygen, while losing nitrogen, until there is collected liquid oxygen with only a trace of nitrogen.

The oxygen gas is delivered to a three-stage compressor which feeds it into seamless steel cylinders under a pressure of 2000 pounds to the square inch.

A steel container of 40-liter (water) capacity contains at that pressure and at 15° C. 6 cubic meters of free oxygen (212 cubic feet). It is connected to the acetylene torch through a two-way diaphragm reducing valve, at a pressure slightly above atmospheric.¹⁷ Each cylinder is closed by a safety angle valve which at all times must be free from oil.

Liquid oxygen is also transported in tank cars, or in tanks on trucks, and delivered to large users. These users draw some of the liquid oxygen from an intermediate tank from which it can be vaporized, and the gas is then compressed into cylinders. The tank carrying the liquid oxygen is a double-walled steel tank with the space between the walls filled with Silocel, pumped out, until the pressure is between .001 and .020 mm.

Nitrogen. The economical way to utilize liquefied air is to make use of both the oxygen and the nitrogen; the oxygen to fill oxygen cylinders, and the nitrogen, which otherwise is lost in four-fold volume, in a special way, as a reaction. This is rarely realized. As a rule, oxygen plants liquefy air, save the oxygen and waste the nitrogen; while the manufacturer of ammonia, for instance, uses the nitrogen and wastes the oxygen. Nitrogen fixation is usually made from producer gas.

Argon. In a plant making nitrogen primarily, the argon will first accumulate with the oxygen; this impure oxygen is fed into a very tall column, rising about half-way up. There passes out at the top, through a dephlegmator cooled by liquid nitrogen, 50 per cent argon with nitrogen. The gas enters a second column with a similar dephlegmator at its top, and at the base argon with an oxygen impurity, while the nitrogen passes

downwards with bells providing liquid seals through which the gases must bubble are in use in some installations. Plates and bells are of copper.

connected to 30 pounds for welding. The construction of the reducing valves or regulator is shown in "Acetylen," by Vogel, p. 240 (see under Acetylene); and in "Oxy-acetylene welding," by S. W. (1916), published by the Industrial Press, New York, on p. 18.

out at the top.¹⁸ The argon is freed of oxygen by passing it over heated copper. Argon is used to some extent to sweep traces of oxygen out of electric light bulbs just before sealing, and in gas-filled lamps.

At atmospheric pressure, argon boils at $-185^{\circ}\text{C}.$ between oxygen and nitrogen.

NEON SIGNS

Neon and several other rare gases in the atmosphere have been put to work in illuminated signs which allow novel and striking effects: the signs are spoken of collectively under the name "neon signs." These luminous signs consist of slender tubing, such as the chemist has long used in the laboratory, bent into the form of letters or figures. They contain a gas at low pressure (12 mm.) through which an electric current of appropriate voltage is constantly passing. This voltage is 6000 to 12,000 volts, the current quantity very small, 25 milliamperes; such current is obtained from the ordinary 120 volt A.C. lighting circuit connected to the primary, taking the high voltage current off the secondary winding of a transformer. Each sign is furnished by the manufacturer with a transformer which delivers the proper voltage. It is now customary for the sign company to sell service rather than the sign and equipment, and to attend to the uninterrupted operation of the signs.

The voltage required depends, among other conditions, upon the particular gas or combination of gases used; this difference reflects the ionization potentials¹⁹ of the single gases, listed in Table 38, with the color they produce, and the amount of the gases in the atmosphere.

TABLE 38.—*Properties of the rare gases of the atmosphere, and of mercury.*

	Ionization voltage 1st electron	Ionization voltage 2nd electron	Color	Parts per million in atmosphere
Helium	24.45	54.12	cream	5
Neon	21.48	40.9	red	15
Argon	15.70	27.82	bluish	9000
Krypton	13.90	26.4	light blue	1
Xenon	12.0	24.25	light blue	0.1
Mercury	10.39	19.0	green blue

Mercury forms part of the gas-vapor system in many tubes, because it carries the current easily, when the tube is "cold," for example, thanks to its low ionization voltage.

The tubing is of lead-potash glass 10 to 12 mm.-diameter. The electrodes are copper, if no mercury is to be part of the tube, or iron, when mercury is used. The area of the electrode was considered an important feature at one time (Georges Claude). Leads sealed in the glass permit connection to outside lines. The electrodes are of sheet metal or woven wire. The tube is shaped over the flame, and its air pumped out through a side sealed-in tee; next the current is passed for some time, with alternate vacuum exhaustion, in order to remove any trace of air. For a neon sign, neon from a one-liter supply flask is admitted by turning a glass-stopcock at the end, reading a mercury gauge, until the pressure reads 12 mm.; this requires

¹⁸ "Die Fluessige Luft," by Kolbe, pages 338 to 343 (Ref. 10).

¹⁹ Ionization potential = potential for molecular distances required for formation of the ion.

seconds. The tube is then sealed off at a previously provided narrowed end. If the cubical content of the sign is 50 cc., it receives $50 \times 12/760 = 8$ cc., so that a one-liter flask suffices for 1250 similar signs. The neon in colorless glass tubing gives an intense, very pleasing red. A small amount of krypton may be mixed with the neon to lower the operating voltage. Mercury in clear-glass tubing gives blue; mercury and argon, a purplish blue. Mercury in amber glass produces green. Other colors will be obtained by the table, still others by combination of colored tubes with different gases. The smaller the diameter of the tube, the greater the voltage required, but the more luminous the column. The tube is continuous, for its total length not over 10 or 12 feet; the parts not wanted are painted in black, and do not show.

The luminous signs may develop at an increasingly rapid rate if the method for efficiency in the transformation of electrical energy into light is improved. The Mazda lamp furnishes 9 lumens per watt; the neon tube 10 lumens per watt. There is the further consideration that the human eye has a sensitivity quite different for the different colors; for example, 10 per cent of green will seem as intense as 90 per cent of red. George E. Eide has found that substituting xenon or krypton for argon in the Mazda lamp increases the light efficiency 33 per cent. Improvements in the electrodes for neon signs have been made; thus hollow tubes instead of rods have proved beneficial. Coating the electrode with easily ionized metallic cesium^{19b} gives good results; thus a tube required 280 volts before coating the electrode and only 70 volts after coating it with cesium. The amount of light delivered by a tube depends upon the amperage, not upon the voltage.

The difference in ionization potentials may result in hiding certain gases from others, for example, 1 part of krypton in 3 million parts helium is readily detected spectroscopically, but 1 part of helium in 2 parts of argon remains undetected.

The vapor of sodium is used for conducting the current and light production, in a double walled tube to prevent the condensation of the sodium, with oxide electrodes to maintain a high current density; a special Jena glass (or "Pyrex" glass) must be employed.^{19c}

Fluorescent Lamps. The Fluorescent Mazda lamps, also called Mazda lamps, have come into wide use. They are tubular lamps (100 watts: 60 inches long, 2½ inches in diameter; 6 watts: 9 inches long, ½ inch in diameter) consisting of a glass tube in which a drop of mercury has been placed, a small amount of argon or other gas, and an electrode at each end. The inner walls of the tube are coated with a fluorescent salt, such as zinc silicate, calcium tungstate, and cadmium borate. Under the action of the electric current, the mercury atoms give out a radiation (among others) in the violet, with wave lengths of 2537 Å; this invisible radiation activates the coating salt which now emits light over a broad range of wave lengths in the visible spectrum. Thus for the salts mentioned, 4500-6200 (green), 4500-7000 (blue), and 4000-7200 Å (pink), respectively. Normal alternating

U. S. Patent 2,065,947, and 1,985,855, to Raymond Nauth.

U. S. Patent 1,984,426, to Marcello Pizani; another patent to the same inventor, also for a lamp, was 1,984,429.

current at 110 to 125 volts is used. The bulb wall temperature, in operation, is about 104° F. (40° C.).

SULFUR DIOXIDE

Of the more compressible gases, chlorine²⁰ and ammonia²¹ are discussed elsewhere. Sulfur dioxide, SO₂, anhydrous, liquefied under a moderate pressure (2 to 3 atmospheres) at room temperature, is shipped in steel cylinders of 50 or 100 pounds capacity, in 1-ton containers, and in single-unit 1-ton ear tanks. It is used from such cylinders and tanks in preparing hydroxylamine sulfate, which in turn serves in making dimethylglyoxime, the nickel reagent; for refrigeration, for bleaching, and, increasingly, petroleum refining (Chapter 24). The boiling point is - 10° C.

The burner gas²² from sulfur (or pyrite), freed from dust, and each is dissolved in water in two towers used in series; the solution from the second tower is elevated to the top of the first tower, where it meets the rich gas. Burner gas with 8 to 12 per cent sulfur dioxide yields a 1 per cent solution. In a third tower this solution is sprayed, at the top, and flows down, while steam is injected at the base of the tower; previously the 1 per cent liquor was heated in a closed coil laid in the spent liquor from the base of the still. The packing in all the towers may be coke, or special earthenware cylinders. The gas issuing from the third tower is cooled to remove most of its moisture, and is passed up a fourth tower down which concentrated sulfuric acid flows. The dried gas is compressed in a bromine pump to 2½ atmospheres, which suffices to liquefy it.

Nitrous Oxide. Nitrous oxide, N₂O, is made by heating ammonium nitrate to 200° C., in small lots (50 pounds) in aluminum retorts. The gas is cooled in a condenser, washed in a solution of sodium dichromate to remove nitric oxide, in caustic to absorb nitric acid, and in water. Under a pressure of 100 atmospheres it liquefies, in small shipping cylinders, for instance, or it may be stored in a gas holder. The reaction is $\text{NH}_4\text{NO}_3 = \text{N}_2\text{O} + 2\text{H}_2\text{O}$. Nitrous oxide is used as general anesthetic,²³ usually mixed with oxygen, and sometimes with ether vapor.

Carbon monoxide, CO, is a combustible gas, but carbon dioxide is not; it forms an essential part of water gas, discussed in Chapter 15. The monoxide may be liquefied with greater ease than hydrogen, and this feature was utilized by Claude in order to separate the two, as discussed in the first part of this chapter.²⁴ Carbon monoxide is poisonous. Carbon dioxide is discussed in Chapter 12.

Acetylene.²⁵ The two important uses for acetylene are the welding and cutting of steel, and lighting. It is made by the action of water on calcium carbide,²⁶ a product of the electric furnace:



²⁰ Chapter 5.

²¹ Chapters 6, 12, and 14.

²² Chapter 1.

²³ Chapter 30, under Pharmaceuticals.

²⁴ "The manufacture of hydrogen by partial liquefaction of water gas and coke oven gas." Gustave Claude, *Ind. Eng. Chem.*, 14, 1118 (1922).

²⁵ "Das Acetylen," J. H. Vogel, published in a series of special books on Chemical Technology. Verlag von Otto Spamer, Leipzig, 1923.

²⁶ Chapter 17.

to a great extent, electricity has displaced the acetylene lighting systems installed in residences and institutions, but for lighthouse purposes, the brilliancy of the acetylene flame has secured its retention in many instances. Acetylene is used for miners' lamps in mines free from explosive gases without screen protection, for instance in rock-salt mines, in gypsum mines, in certain coal mines. Acetylene is also the raw material which may be made into acetaldehyde, alcohol, acetone, and rubber, as described in chapters 25 and 39.

In generators which are stationary the construction is usually such that when the drawing of the gas stops, the accumulating new gas depresses the old gas away from the supply of carbide, as indicated in Figure 114. In the miner's lamp an adjustable flow of water passes drop by drop from an upper reservoir to the carbide store below. A third principle is to drop the carbide grains into a store of water. Many forms of generators are portable and may be moved about the shop; the gas generated may be under high pressure (6 pounds), or low pressure (one-third pound or so). In addition to generators, acetylene tanks furnished by a manufacturer are frequently used; they require no installation; the cost is twice that of the generated gas (leaving out interest on the generator).

In acetylene tanks, the gas is not simply compressed, but dissolved in acetone. The reason is that acetylene alone under the pressures higher than one atmosphere tends to decompose explosively; dissolved in acetone, it may be compressed under pressures of 10 or 15 atmospheres with safety. The capacity of the

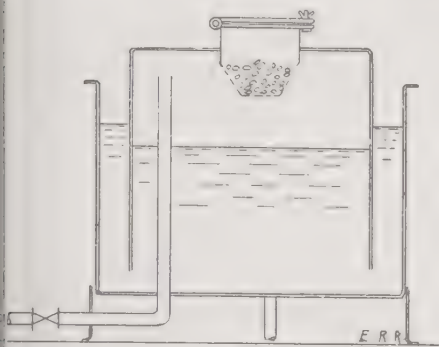


FIGURE 114.—Acetylene generator, stationary type (after Vogel).

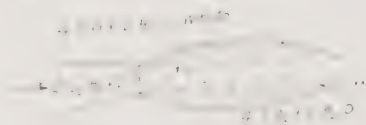


FIGURE 115.—The oxygen acetylene flame (after Vogel).

ordinary tank (40-liter volume) is about 200 cubic feet of free acetylene. In addition to the acetone, some tanks contain a porous solid filler, such as hardened (by heating) wood charcoal. In order to fill the cylinders, the acetylene gas is dried over fused calcium chloride, and compressed in a compressor (60 r.p.m.) liberally lubricated with glycerin. The compressor is built to withstand ten times the maximum gauge pressure (15 atmospheres). Several cylinders are connected at one time to the compressor and occasionally shut off to allow time for the solution in acetone. There are two kinds of welding torches, high pressure and low pressure, differing in important details. Cutting torches differ from welding torches in the following way: in addition to the oxygen and acetylene conduits,

which both torches have, the cutting torch receives a stream of oxygen around the flame; it is this oxygen which cuts the steel, by oxidizing it and forcing away the particles of oxide formed; the flame serves merely to attain the oxidizing temperature. The flame in each has an inner brilliant part whose temperature is estimated at $3000^{\circ}\text{C}.$; in the welding torch this is surrounded by a larger envelope into which the air penetrates. The inner portion, which does the welding, is sometimes called the neutral flame. (Compare Fig. 115.) The use of acetylene is not without danger, and the directions and cautions of the manufacturer must be observed.

Other, cheaper sources of acetylene are actively sought; one, for example, is a natural gas which is pyrolyzed under reduced pressure, or a natural gas passed over a highly heated refractory.^{26a}

WELDING BY THE ATOMIC HYDROGEN FLAME

A welding torch has been developed in which atomic hydrogen, produced by passing hydrogen through an electric arc, is produced at the torch tip and furnishes the heat for welding as it combines to form molecular hydrogen. The temperature is as high or higher than that of the electric furnace; it is estimated as between 4000° and $5000^{\circ}\text{C}.$, so that materials hitherto considered infusible may be fused. The weld produced may be worked as readily as the original sheet. This flame has the additional advantage that it is non-oxidizing and non-carbonating.²⁷

Production. Table 39 gives the production of compressed gases. Very small quantities of these gases processed at once are not reported.

TABLE 39.—*Production of compressed gases.**

	Cubic feet	Value per 1000 cubic feet
Hydrogen	1,124,168,000	\$ 1.38
Oxygen		
by liquefaction	4,452,209,000	
by electrolysis	109,759,000	5.28
Acetylene	1,274,164,000	13.00
Nitrous oxide	95,577,000	9.00
	Pounds	Value per pound
Carbon dioxide, liquid	102,208,118,000	.04
Dry Ice	356,893,516,000	.0155
Ammonia, anhydrous	227,219,049	.0374

* Bureau of the Census.

OTHER PATENTS

U. S. Patent 1,850,529, extraction of helium from natural gas, wherein its percent is comparatively small; 1,881,115 and -6, helium from gaseous mixtures which have boiling points above the critical temperature of helium; 1,772,202, extraction of krypton and xenon from liquid oxygen, by increasing the concentration, then passing through an absorbent for krypton and xenon; 1,892,186, production of argon and neon as by-products in the synthesis of ammonia from atmospheric nitrogen; 1,872,515, production of dry acetylene from calcium carbide and effecting complete hydration of the carbide; 1,794,004, production of acetylene and hydrogen in the electrolysis on isolation of argon, Brit. Patents 218,266 and 226,783 (1924) and U. S. Patent 1,420,000.

Knowles' patents, on electrolysis of water: 1,067,822, apparatus for purifying electrolytic gases by combustion; 1,566,543, electrolytic cell, automatic control of liquid level.

^{26a} U. S. Patent 1,983,992.

²⁷ "Flames of atomic hydrogen," Irving Langmuir, *Ind. Eng. Chem.*, 19, 667 (1927); *or. Chem. & Electric Review*, 29, 153 and 160 (1926).

electrolytic cell and washing of the gases evolved; 1,485,461, electrolytic cell for the production of H_2 and O_2 by electrolysis of water; 1,866,472, electrolytic apparatus for washing gases evolved from a cell by causing them to bubble through water; 2,118, electrolytic apparatus using thicker sleeve around the electrode on the sides along the opposite electrode in order to maintain a high purity gas; 1,856,393, temperature controlling system for electrolyte in electrolytic cells; 1,767,292, gas washer electrolytic apparatus by bubbling gases through chambers containing the washing fluid; 1,767,375, washing gases by bubbling them through chambers containing the washing fluid; 1,821,018, electrolytic apparatus for electrolysis of liquids for production of gases.

PROBLEMS

In the steam-iron process for hydrogen, the retorts as given in the text produce 1 cu. ft. per hour. Over the day, how many hours are all the retorts in actual operation making hydrogen? Disregard purging period. If 3 times the amount of dry steam is taken, what is its weight?

In the installation of 306 Knowles cells given in the text, let the current efficiency be 100 per cent, and let the operating voltage be 2. What is the energy efficiency? Compare Chapters 5 and 18. For the production of hydrogen gas as described, how much distilled water will be required?

Let the "parts per million" for the rare gases in the atmosphere represent volume. How many cu. ft. of air will be required in order to prepare 1 liter of each of the rare gases? The first operation for liquid oxygen has a 90 per cent yield; what is its rare gas content is the same as in the original air. The recovery on the second operation may be taken as 80 per cent.

An acetylene generator receives a charge of 250 pounds of calcium carbide, 90 per cent CaC_2 . What is the volume of acetylene gas which may be generated, measured at ordinary temperature and pressure?

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A number of chemical industries depend upon the existence of micro-plant organisms, so small that they are visible only under a high-power microscope; they are therefore called micro-organisms. Under the proper conditions, they grow at enormous speed; they have the power to consume (apparently) one substance and to produce another, and it is this function which makes them valuable. In these industries, the chemist works hand in hand with the bacteriologist.

Chapter 20

Processes Based on the Activity of Yeasts and Bacteria

From time immemorial, one of the processes which depends upon the existence and growth of micro-organisms has been practiced, namely, the alcoholic fermentation of grape juice and fruit juices, but the exact nature of the process remained a mystery until Louis Pasteur discovered, isolated and classified the several kinds of organisms. He succeeded in demonstrating that fermentation and bacterial disturbances in general were not due to spontaneously generated plant organisms, but to organisms which already existed elsewhere and which were carried in by air currents,¹ on the surface of the fruit, or in other ways. At the same time, the nature of the festering of wounds became clear; as a result, the modern science of antiseptic treatment was born.

The transformation of certain sugars, the monosaccharides, such as glucose and fructose, into alcohol, is brought about by yeast; carbon dioxide is evolved profusely at the same time, so that the liquid seems to boil.² The formation of lactic acid is due to a bacterium. The place of these organisms in the complete group will be clearer from some general considerations.

Yeasts, bacteria, and molds are fungi, vegetable growths. Yeasts multiply by budding, with or without spore formation; bacteria multiply by division or fission, in rare cases by spores. Yeasts show a definite nucleus under the microscope, whereas bacteria do not. Yeasts are commonly spherical, and about 0.01 mm. in diameter; bacteria are long or short rod-shaped, and in general, smaller than the yeasts (about one-tenth the size of yeasts). Bacteria and yeasts differ from molds in that the former are unicellular, while the latter is multicellular. Molds multiply by sporulation. Protozoa are the lowest form of animal life; they are unicellular, and are found in ditch water (amoeba).

The yeast cell contains complex organic substances called enzymes, whose characteristic is that they catalyze a chemical reaction; the reaction which they catalyze is the same as the one the cell as a whole catalyzes. As a yeast cell contains a number of different kinds of enzymes. In industrial fermentations, the enzyme is not isolated; the cell is cultivated and used. For the growth of the alcoholic ferment requires sugars, a small amount of min-

¹ Pasteur had to ascend the Alps many hundreds of feet above human habitation, before he found air which would not contaminate his test solution (veal broth).

² Hence the name fermentation, from the Latin word *fervere*, to boil.

³ The long rods are bacilli; the short ones, bacteria proper.

phosphates, and nitrogenous matter; the effort of the manufacturer to grow yeast, for 1 gram of pure yeast requires 1 gram of sugar, hence there would be no production of alcohol, but rather to produce enough yeast to catalyze the alcohol-forming reaction. Some growth takes place, but the main part of the conversion is due to the action of the dead cells.

Yeasts and bacteria grow best and work best at definite temperatures which vary with the several organisms, but which lie not far from room temperature, perhaps between 5° and 40° C.; 60° is fatal to most of them. Generally the working range for bacteria is narrower than for yeasts. These microscopic plants are carried about by every gust of wind, so that it is difficult to keep any one batch of liquid free from contamination. In order to control the action, all organisms already in the material are destroyed by preliminary heating, called sterilization; after cooling, a pure strain of desired organism, grown under protection (aseptic conditions), is introduced; this is called inoculation, or seeding. Not only the temperature, but the acidity has an effect on the activity (and growth) of the organisms; lactic ferments work well in an acid medium, while most of the bacteria are inactive; on the other hand, too high a concentration of alcohol will destroy the yeast itself. In order to grow, yeast requires air; it causes fermentation best out of contact with air.

INDUSTRIAL ALCOHOL

Fruit juices are fermented and distilled, to concentrate the alcohol and, for the production of potable spirits whose value lies largely in the characteristic of the particular fruit used; the finished liquor purely betrays the origin. It is different with industrial alcohol, for this must be as near chemically pure as possible, and must bear no marks of original material. Industrial alcohol is ethyl alcohol, 95 per cent. The uses for industrial alcohol must be cheap, otherwise the uses will be limited; preferably by-products of other industries are sought. In the United States and in England, the chief raw materials are cane-sugar molasses and beet-sugar molasses; in France, sugar beets, and beet-sugar molasses; in Germany, potatoes, lately also beet-sugar molasses. Any raw material may be used, such as corn⁴ and other grains; these are, however, generally more valuable for food purposes. The liquor from the wood-pulp digester has been made into alcohol, and wood and sawdust have been used in experimental plants. In order to prevent the diversion of industrial alcohol to potable alcohol uses, it is denatured by adding some material which is not easily separated by any physical or chemical process and which renders denatured alcohol unfit for use as a beverage. A number of different formulas are authorized by the Government, so that the industrial user may select the particular formula which will have the least effect upon his particular process (*see p. 345*).

For molasses, the process is essentially fermentation, followed by distillation. For potatoes and grains, the starch must first be rendered soluble by

using damaged corn, a fairly cheap raw material may be obtained: 1 ton of corn (33 bushels) yields 100 gallons of 95 per cent alcohol; at half the normal price the raw material would be about 50¢ per gallon. For other prices, *see further*.

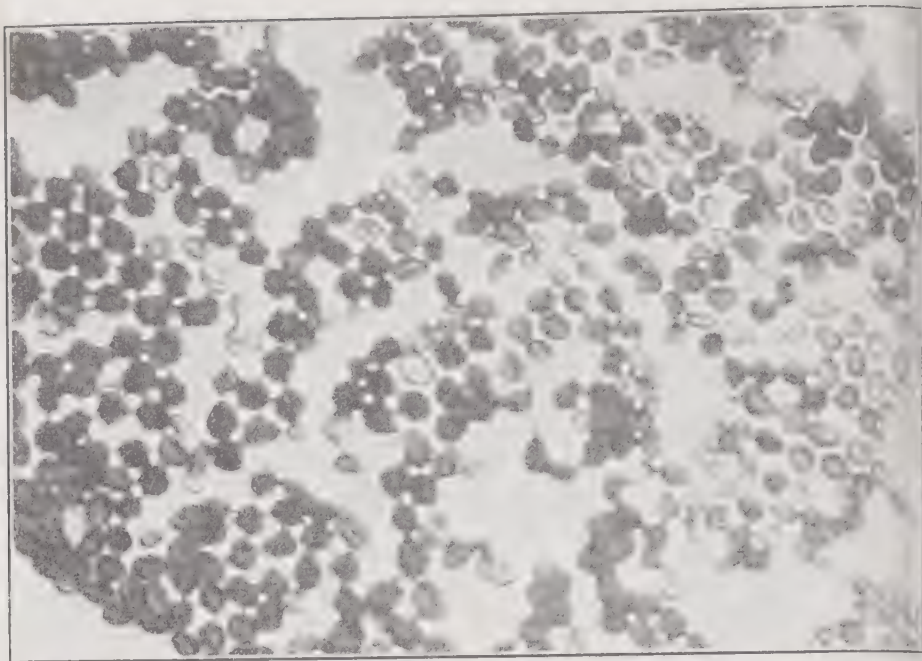


FIGURE 116.—Yeast cells, magnified 300 times. The light cells are the disintegrating ones; the dark cells the growing ones. The inter-connection between mother and daughter cells is shown in the lower left; in several places, a cell with bud formation is visible.

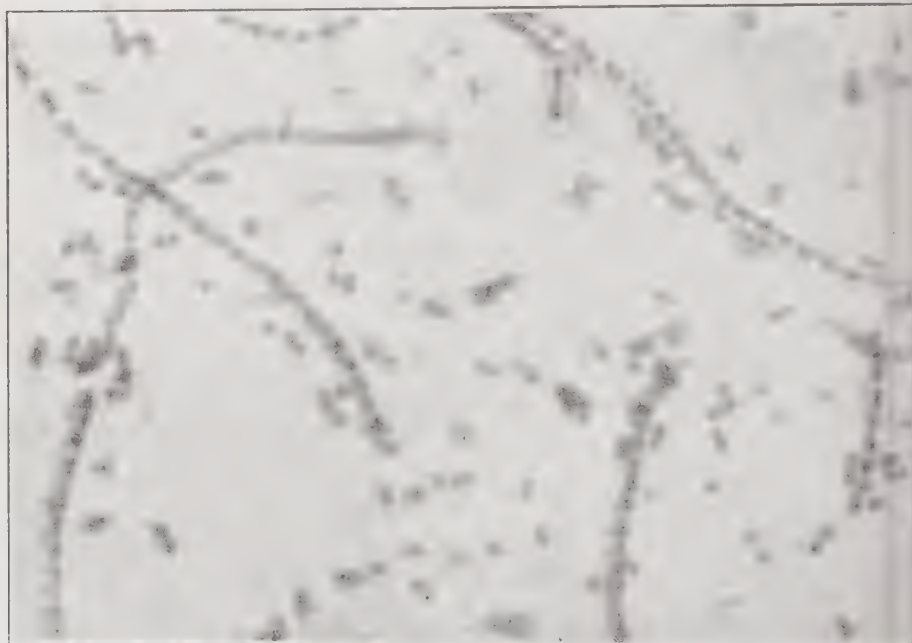


FIGURE 117.—*Bacterium lactis acidii*, used for the production of buttermilk, magnified 1800 times.

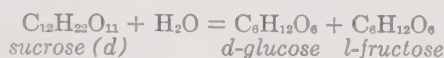
ing; the water extract containing the dissolved starch, the wort, is fermented, and the fermented solution distilled.

Alcohol from Molasses. Molasses is well suited for the production of methyl alcohol, (C_2H_5OH) for it contains sugar⁵ in a form which admits direct fermentation by yeast; the absence of hulls or peels also simplifies the process. Molasses is the final mother syrup in the crystallization of table sugar, or crystal sugar; 15 to 20 per cent of the sugar in the sugar beet, or cane, cannot be crystallized without special installations, because the accumulated non-sugars prevent crystallization.⁶ Molasses from the sugar cane differs somewhat from the beet sugar molasses, as shown in Table 40.⁷

TABLE 40.—*Analysis of typical cane and beet molasses.*

	Cane molasses	Beet molasses
	Per cent	
Water	20	20
Sucrose	30	50
Raffinose	0	present
Invert sugar	32	trace
Ash	6	10
Organic non-sugars	12	20

Sucrose is the crystal sugar, and is the same substance, whether made from the sugar cane or the sugar beet; it is a disaccharide, $C_{12}H_{22}O_{11}$. It is converted by invertase, an enzyme present in the yeast, into two molecules of monosaccharides, with the addition of water:



The monosaccharides, glucose and fructose, are attacked by the enzyme invertase, the most important enzyme in the yeast, and are changed into alcohol and carbon dioxide. Invert sugar consists of equal parts of d-glucose and l-fructose.

The molasses is received at the alcohol plant in the form of a thick, syrupy mass, transported in tankboats holding from 1 to 2 million gallons; another method, which is less common, is to concentrate the molasses in a vacuum pan, and to run the concentrate into cast-iron, water-cooled molds, where it solidifies to a loaf. The mold is previously lined with paper which adheres to the loaf and protects it against moisture absorption. Wooden molds are now rarely used.

The molasses is diluted with enough water to produce a solution or "mash" containing about 10 per cent sugar. A nutritive solution may be added to the mash after dilution, providing there is insufficient yeast food in the molasses. With cane molasses a small amount of sulfuric acid is added (about one gallon of concentrated acid to 4000 gallons mash) in order to produce a slight acidity which retards any bacterial action. With beet molasses it is necessary first to neutralize the mash and then add sulfuric acid, as in the case of cane molasses. The yeast requires a slightly acid medium for its most vigorous growth. If desired, the bacteria in the

⁵The chemist distinguishes many kinds of sugars; sucrose, glucose, and fructose are discussed in this chapter; raffinose is a tri-saccharide, with C_{18} ; see Chapter 23.
⁶The limit is 60 parts sugar to 40 parts non-sugars.
⁷Chem. Met. Eng., 16, 437 (1917).

original molasses may be killed by sterilization, in which case it is necessary to be sure that the mash is not alkaline. Cane molasses require no acid if sterilized.

Previous to this mashing, the laboratory has prepared yeast in sufficient quantity to inoculate the mash; about 5 per cent in volume is required for proper fermentation. The mash is brought to the proper temperature, and the yeast added. Considerable heat is evolved during fermentation, causing the temperature of the mash to rise. This should be controlled so that the final temperature never goes above 100° F. (37.8° C.). If there is no cooling available, such as coils immersed in the fermenting vats, it is necessary to cool the mash before adding the yeast. The proper starting temperature can be determined only by experimenting, but it is usually around 70° F. (21° C.). The time required for complete fermentation is about three days.

In about three hours' time after adding the yeast the evolution of carbon dioxide can be readily observed. The amount of this gas gradually increases, until at the end of 24 hours the entire mash appears to be in motion. During the early stages of fermentation the yeast grows and then proceeds rapidly to convert the glucose and other monosaccharides into alcohol. At the same time, the enzyme invertase in the yeast is converting the sucrose into monosaccharides.

The fermentation vats are commonly made of steel but may be made of any material which can be readily sterilized. Wooden vats were used in some of the older installations. The yeast tanks, like the fermenting vats, must be constructed of material which can be easily cleaned and sterilized. Enameled iron is best.

The principal reaction during fermentation is:



Other products formed are higher alcohols, called fusel oil (of which amyl alcohol is the principal one), glycerin, and a small amount of organic acids.

The carbon dioxide evolved from the fermentation may be collected by covering the fermenters and piping the gas away. The gas is usually purified by scrubbing with water to recover the alcohol contained therein, then passing the gas through an adsorbing material such as charcoal to remove the odors. It is then compressed and bottled in steel cylinders as liquid carbon dioxide, or made into the solid.⁸

The product of the fermentation is a weak alcohol, which must be concentrated; this is followed by rectification. The final product is 95 per cent alcohol. The yield is about 0.4 gallon (U.S.) per gallon of molasses, and, as shown in Table 40, and this represents about 90 per cent of the sucrose converted to alcohol. The loss is due to alcohol vapors⁹ which escape from the fermentation vat, and to side fermentations which produce other substances than alcohol. The residue from the distillation is a more or less clear liquid which may be concentrated and evaporated to dryness for

⁸ Chapter 12.

⁹ In the installation with carbon dioxide recovery, this alcohol is saved.

ssium salts which it contains.¹⁰ The yeast remains in the liquor and is re-
 yed. In the larger plants, it is customary to run a smaller fermenta-
 plant expressly to obtain yeast in pure cultures; the procedure is some-
 t different from the main fermentation. The species of yeast best
 d is taken from the surface of the sugar cane.

Alcohol from Grain and Potatoes. The method of making alcohol
 a grain and potatoes includes not only the fermentation described under
 sses, but also a preliminary treatment designed to dissolve the starch,
 source of alcohol in this case, and to hydrolyze it, by enzymes, to a
 of sugar which can be attacked by yeast.

This preliminary treatment will involve a reduction in size to a meal,
 a mashing period similar to the corresponding operations under
 very Industry," but generally on a larger scale. The fermented liquor
 ncentrated in a plate column called the "beer still," like all columns at
 stage, whose plates do not have bubble caps, but sieve bottoms which
 it the gradual descent of the liquor with its suspended solids. The con-
 rated alcohol vapors pass out at the top of the column still and are
 ensed; the concentrated alcohol so obtained, containing about 50 per
 alcohol, is rectified as described further on. The waste from the still is
 d "slops."

Potatoes are handled in a similar way and mixed with malt in the pro-
 ons of 2 pounds of malt to 100 pounds of potatoes, while for corn, 8
 ds of malt are taken for each 100 pounds of the grain.

Malt is made in a preliminary operation, by the controlled (partial)
 ination of barley. The barley is first steeped in cold water, then
 ed on the floor in the air, and occasionally turned over; the tempera-
 rises, oxygen is absorbed, and carbon dioxide is given off. The germ
 n the barley, the plumule or arospire, grows by this process, and con-
 the desired soluble ferment, the diastase. Such malt, crushed between
 es and mixed with some water, is the agent which alters the dissolved
 h to the sugar, maltose. About four-fifths of the starch in the potato
 tained in the wort, as maltose solution. Instead of malt, mineral acids
 be used.

he dilute alcohol from the fermenting vats (7 to 12 per cent) is con-
 ated by distillation in an apparatus with continuous operation.

CONCENTRATION AND RECTIFICATION IN A SINGLE, CONTINUOUS SYSTEM

One of the earliest and best-known methods for the continuous distilla-
 and rectification of the fermented liquor, with complete separation and
 eation of the 95 per cent alcohol and by-products, is that of Emile
 aume.¹² This process has been modified and improved in the inter-
 ing years, and others invented, but inasmuch as it illustrates principles
 on to all, it will be described here.

the Guillaume Process. The essential parts of the Guillaume process
 own in Fig. 118. The apparatus consists of a boiler (not shown), the

he still residue is first concentrated at 32° Bé., and this thick liquid supports its own combustion
 al furnaces; the ash contains the potassium. The primary purpose of the operation is to dispose
 enormous amount of waste liquor. See Chapter 8.
 S. Patent 887,793 (1902).

rectifying column *A*, the purifying still *B*, a vessel *C* to maintain a given alcoholic content, a distilling column *D* for exhausting the charge, alcohol still *E*, dephlegmators, condensers, and auxiliary apparatus. There is no connection between still *B* and column *D*; a solid metal plate separates them. They are superimposed merely for convenience.

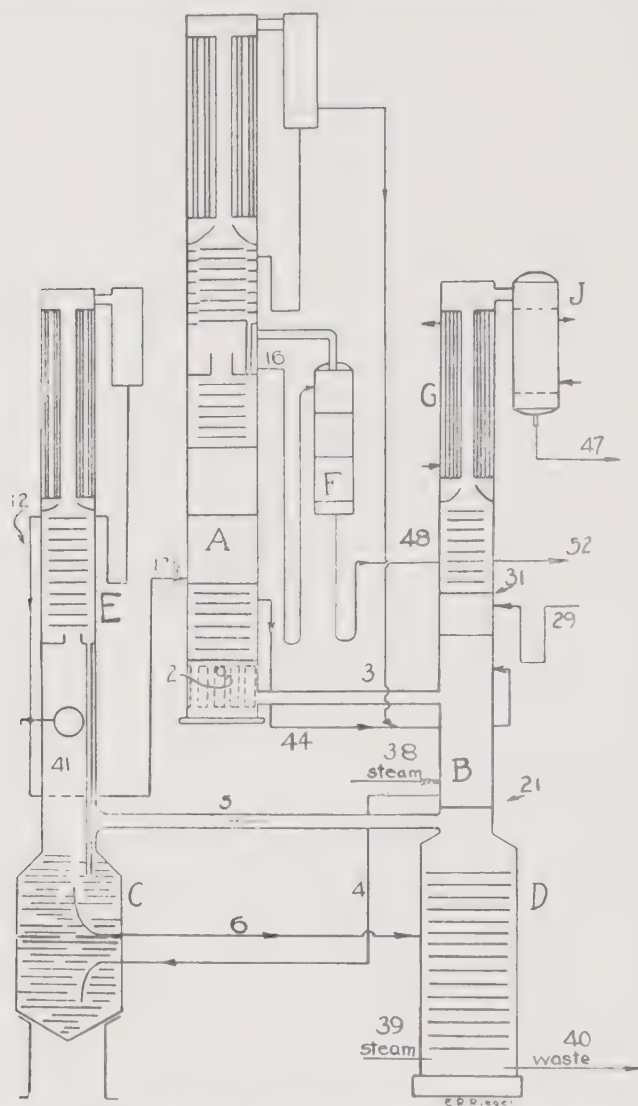


FIGURE 118.—The Guillaumet process, for the concentration and rectification of beer by continuous operation of the beer from the fermenting vats. *A*, rectifying still; *B*, purifying still; *D*, weak alcohol still; *E*, open still supplied by alcohol column. *C*, storage vessel for hot hydrous alcohol. (See text for other parts.)

The crude alcoholic vapor from the boiler enters the internal drum 2, in the bottom of still *A*, merely passing through on its way to still *B* through pipe 3. This drum is the source of heat in *A*.

All of the boiler vapor arrives in *B*; it is merely somewhat cooler, partly liquefied. A portion travels down the plates of this column, to form an entering supply of live steam (entering at 38). The condensate (aldehydes and all volatile impurities, and reaches the bottom of *B*). This condensate is almost pure. It is conveyed through pipe 4 to the storage vessel *C*.

In *B*, the volatile impurities travel upward, being at the same time fractionated. A regulated stream of water is added at 29, in order to dilute alcohol sufficiently to hold it back. The fusel oil is drawn off at 31, to be fractionated further in a separate apparatus; this fraction contains amyl alcohol, amyl valerate, ethyl acetate, ethyl isovalerate, ethyl butyrate, and other bodies. Escaping condensation in the dephlegmator *G*, the aldehydes and formate esters pass into condenser *J* and from there, now liquid, into receiving vessels.

By adding water at 29, the various esters and higher alcohols can be disengaged away from the alcohol without any great amount of alcohol distilling. This is because the esters and higher alcohols are comparatively insoluble in water and do not suffer a reduction of vapor tension due to water admixture as does ethyl alcohol.

The purified, weak alcohol in *C* is delivered at a continuous rate to the column *D*, where it travels downward over the plates, meeting live steam which enters the column *D* at 39. There passes out of *D* to the open column *E* vapor containing all the alcohol and considerable water; it reaches column *E* where it is condensed, fractionated and concentrated in the usual manner.

The product from *E* is 86 per cent alcohol, still purer than when it entered vessel *C*, for a small amount of amyl alcohol is removed from the upper plates and sent to 48; it leaves *E* at the upper plate through line 12 and goes to the bottom of still *A*, where the final rectification to the full strength takes place. A weak residue passes out of *A* through pipe 44 and is returned to the system at still *B*. The strong alcohol leaves *A* through pipe 16. It is passed through a supplementary column for a final purification of such esters as were formed during the process of distillation, by means of fractionation and esterification.

The flow of the various liquids is regulated by valves and a control mechanism located in open still 41, and depends upon the temperature of the various streams.

In one of the more recent continuous processes for the production of 95 per cent alcohol, the addition of water is avoided; only water-vapor in the form of steam is injected. Proper operation is insured by the temperature selected point, about two-thirds of the way up, 85° C., under which condition the vapor passing out at the top of the still will be 95 to 96 per cent alcohol. Should the temperature go higher, a larger amount of condensate from the condenser above the still is returned to the still; should it go lower, the amount of the same cold liquid is decreased.¹³

The concentration of aqueous alcohol is possible because when it is vaporized the vapor is richer in alcohol than the liquid from which it rises (see page 119). There is at each plate of the still an enrichment of the vapor, which rises to the next plate, there to gain in alcohol again, while the liquid descends, to meet on the lower plate a leaner vapor to which it adds alcohol. The paths of vapor and liquid are counter-current. Pure ethyl alcohol (ethyl alcohol, C_2H_5OH) boils at 78.5° C., water at 100° C.; in the case of an aqueous alcohol, the gain in alcohol in the vapor continues until 97.2 per cent by volume is reached; beyond that the vapor no longer

differs from the liquid from which it rises (constant-boiling mixture boiling point $78.174^{\circ}\text{C}.$); for this reason, 97.2 per cent alcohol is the highest strength obtainable by distillation alone. Industrial alcohol contains 95 per cent alcohol; the remainder is water.

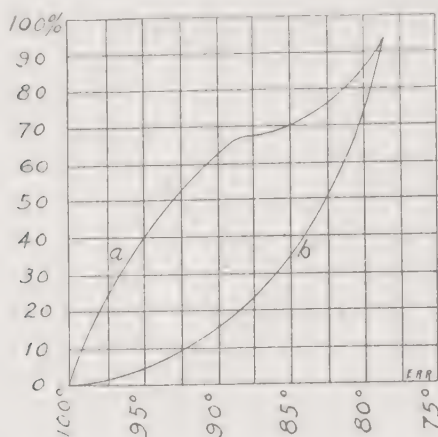


FIGURE 119.—Difference in composition between the vapor and the liquid for alcohol-water mixtures. Abscissas, boiling temperatures; ordinates, percentages of alcohol in *a*, the vapor; *b*, the liquid. Example: At $90^{\circ}\text{C}.$, the liquor has 16% alcohol, but the vapor rising from it has 62%.

"100 U. S. proof" contains 50 per cent alcohol; "200 proof" is 100 per cent alcohol. The "100 British proof" is slightly stronger than the 100 U. S. proof. Alcohol of 100 U. S. proof will burn when touched with a match.

Synthetic ethyl alcohol is made from ethylene or from acetylene (see chapters 24 and 25).

COST AND USES OF INDUSTRIAL ALCOHOL

Alcohol has so many uses in the industries and in the arts that it can be said to be indispensable. This is reflected in its production figures. Some of the uses depend upon its chemical nature, and no other substance could be substituted; chief among these is the manufacture of ether.¹⁴ Other chemicals are made from alcohol, although they could be made from other raw materials; chloroform is an example. The perfume industry makes use of the solvent power of alcohol for essential oils; no suitable substitute is known. Certain flavoring extracts (vanilla) similarly require alcohol as solvent, as do furthermore the lacquer, Celluloid, smokeless powder, and other industries. Alcohol serves also as a fuel, in lamps and burners, in the form of a liquid and of "solidified alcohol,"¹⁵ and in internal combustion motors; the latter use is susceptible of considerable development which will depend upon the supply of crude oil and gasoline, and on the price of alcohol.

TABLE 41.—Ethyl alcohol production in the United States* for fiscal year ended June 30, 1941.

Amount and kind of material used	Alcohol, proof gallons	Per cent of total
220,596,526 gallons molasses	210,426,805	70.41
53,399,664 gallons ethyl sulfate	69,902,800	23.39
189,118,727 pounds grain	17,532,441	5.87
Total alcohol produced	298,845,417	100.00

* U. S. Treasury Dept., Bureau of Internal Revenue, Alcohol Tax Unit.

¹⁴ Chapter 30.

¹⁵ U. S. Patent 1,208,265, to C. Baskerville. The proportions and ingredients are 10 to 15 per cent saturated calcium acetate solution, 85 to 90 per cent industrial alcohol, 0.5 to 1.0 per cent stearic acid.

The cost of alcohol depends upon the cost of the raw material, on the cost of fuel,¹⁶ and on the efficiency of the fermentation. If molasses costs 25 cents a gallon, which would be high, and $2\frac{1}{2}$ gallons of molasses are required to make 1 gallon of alcohol, the usual yield, then the latter must cost 25 cents for raw material alone. The cost of converting molasses to alcohol is about 4 cents per gallon, as deposited in storage tanks. There is an additional cost of about 4 cents for overhead and for labor and materials required in denaturing, barreling, shipping, etc. The selling price of alcohol during 1941 was in the neighborhood of 45 cents per United States gallon; a "ceiling" was set late in 1941 at 50 cents a gallon f.o.b. by the Office of Price Administration, since ethyl alcohol is an essential material. In Germany the price is less, because of a state subsidy. It has been estimated that with wood waste as a source, a much lower cost could be reached.¹⁷

In nearly all countries, ethyl alcohol for industrial purposes may be sold tax-free; in order to prevent the diversion of such alcohol to beverage uses, certain distasteful, even poisonous, substances are added. In the United States, there are two classes of denatured alcohol: completely denatured, which may be sold without a permit, and especially denatured alcohol. The standard denatured alcohol for radiators contains, to 100 parts, 80 per cent ethyl alcohol, 5 of isopropanol, 0.75 of aldehyde A, 0.75 of acetate, 0.25 of terpineol (1933). The quotation for completely denatured alcohol, *Formula No. I*, was 44.3 cents a gallon in drum lots (54 drums), in June, 1937. Aldehyde is the name given a liquid made by blowing air through boiling kerosene. There are over 30 specially denatured alcohol formulas suitable for specific purposes. These are sold to manufacturers who may select denaturing materials which have no effect upon particular processes.

BREWING INDUSTRY

Beer is made by boiling in the presence of hops certain extractable materials contained in malted barley and other grains, and then fermenting this mash by the addition of brewers' yeast. The methods employed by brewers in the preparation of beers and ales differ in important details in the various establishments, yet they are sufficiently similar to be represented by a process practiced in a selected brewery in upper New York State, which will be described.

The capacity of the plant is 269,000 barrels per year (1 barrel=31 gallons). The raw materials are rice, corn grits, both of them oil-free, wheat, sometimes soybean, malt, hops, and some others in smaller quantities. Besides these, pure yeast and an abundance of water are required in making the beverage itself and for cooling. The corn grits, which must be free from germ, and the rice, for example, are taken in quantities

The fuel required is estimated at 11 pounds of coal per gallon.

The residue from the wood used would be the fuel, involving no additional cost. "Wood waste as a source of ethyl alcohol," G. H. Tomlinson, *Chem. Met. Eng.*, **19**, 552 (1918); see also *Chem. Met.*, **1**, 558 (1919), and the chapter on the manufacture of alcohol from waste wood and sulfite cellulose in "Industrial Alcohol," by J. G. McIntosh, revised by H. S. Stocks, published 1923 by Greenwood and Son, London. It would seem that the cellulose proper is not the source of alcohol; residue of 65 per cent of the wood used is left, corresponding closely to the cellulose present; see p. 183, in the book of McIntosh and Stocks. Soft woods give 25 gallons per ton, hard woods 10. Note furthermore the Bergius process, chapter 16.

sufficient to furnish 30 to 40 per cent of the required starch, while malt is added to furnish the balance. After passing cleaners and crumblers, the rice and the corn, made up with water, and with the addition of some malt, are heated in a pressure cooker with an agitator under 5 psi pressure for 45 to 60 minutes. The action is mainly the liquefaction of starch. The main portion of the malt, made up with water, is placed in a mash tub, which is just like the cooker, and thoroughly mixed at a temperature between 100 and 120° F. and then allowed to rest. During this period the proteolytic enzymes begin to degrade the malt and other proteins into soluble forms. After this period the contents of the cooker are added to these raise the temperature to 149 to 158° F., at which point the mash is held for conversion. The temperature is then raised to 167° F., which is high enough to arrest the action of the conversion. The purpose of mashing is first to extract from the malt its starch and ferments, including diastase, which changes the starch to sugars during the conversion period. The material next passes to the Lauter tub whose bottom has slots through which the clear liquor, or wort, passes while the arms of the agitator rotate slowly. "Sponge water" in spray form is introduced to exhaust the malt.

TABLE 42.—Analyses of brewery products, November, 1938.

	Indian Head Lager	Indian Head Ale
Appearance on arrival	clear	clear
Color	5.75° Lovibond	6.0° Lovibond
Odor	Pure	Mildly aromatic
Taste	Pure, somewhat full-bodied, good hop flavor	Pure, vinous, good hop flavor
Foam-keeping capacity	Good	Good
Specific gravity	1.01598	1.01399
Saccharometer indication	4.07° Plato	3.57° Plato
Alcohol, by weight	3.80%	4.20%
Alcohol, by volume	4.89%	5.40%
Extract	5.79%	5.49%
Sugar	1.63%	1.54%
Dextrin	2.52%	2.23%
Unconverted starch	None	None
Acidity as lactic	0.16%	0.16%
Protein	0.40%	0.42%
Heavy metals	None	None
pH value	4.60	4.30
Carbon dioxide, 2 bottles	0.48%, 0.48%	0.45%, 0.45%
Original gravity	13.1° Plato	13.6° Plato
Real degree of fermentation	55.8%	59.6%
Apparent degree of fermentation	68.9%	73.8%
Chilling test, clarity (absolute turbidity) on 2 bottles chilled 24 hours in ice pack	a.—0.0029.	b.—0.0030 a.—0.0028. b.—

on the screen ("sparging"). The wort is run into the boiling kettle jacketed copper kettle with capacity, in this plant, of 450 barrels. During the period of boiling, which lasts 2½ to 3 hours, the hops are added at intervals. While in the kettle the enzymes are destroyed, the hop "bitter" is extracted, undesirable proteins are coagulated, other proteins are precipitated by the tannin in the hops, and the whole is sterilized by the heat. There is also a concentration of about 10 per cent. The material is

ed to remove all solids, especially the spent hops, and the clear liquor, settling for a while in the hot wort tank, is run over coolers such as sandlot, and from there to fermenters which may be of wood, glass-steel, or aluminum. Here the yeast is added, for example, $\frac{3}{4}$ pound yeast per barrel. The fermentation lasts seven to ten days, after the beer is run through a cooler into glass-lined storage tanks which s plant have a capacity of 35,000 barrels. Here some 5 to 15 per of beer in high state of fermentation is added to the fully fermented and is allowed to work out; as it ferments it provides the carbonation, e tank is sealed to a pressure of 6 to 8 pounds. The beer absorbs the n dioxide. After a period of a week or more the beer is filtered gh a mass filter under pressure; it is recarbonated sufficiently while g through the pump, at a temperature of 32° F., to bring the carbon e content to 0.48 per cent in the final beer, and the product is bottled ealed. The carbonation may be performed entirely by pumping sterile n dioxide into the cooled beer from the fermenters. The bottled beer eurized at 140° F. (60° C.) after capping.

ABSOLUTE ALCOHOL ON A COMMERCIAL SCALE

In addition to industrial alcohol, there is now on the market, in drum and carload lots, 100 per cent ethyl alcohol, called absolute alcohol. This material has properties of miscibility which industrial alcohol does not possess. In making a motor fuel from gasoline and alcohol, 95 per cent alcohol may be used, it is true, but only by introducing a third component, such as benzene (= benzol), ether, or Tetralin (Chapter 25). Without this component, industrial alcohol does not mix with gasoline. Absolute alcohol does not require a blending agent; it is miscible with gasoline in all proportions.

Such blended motor fuels are of no economic interest in the United States, where gasoline is abundant and cheap, but they are important in countries which must import their petroleum products. Even in the United States there have been proposals to add 5 per cent alcohol to gasoline, as an "emergency relief" measure; to date, they have come to naught.

The second important demand for absolute alcohol comes from the lacquer industry, in which it is a valuable solvent.

Thanks to several continuous methods, absolute alcohol is obtainable at a very reasonable price.

The Keyes Process. In the process patented by Donald B. Keyes,¹⁸ the advantage is taken of the fact that on addition of a third constituent such as benzene (= benzol) to the alcohol and water present in 95 per cent alcohol, a three-constituent mixture, or ternary mixture, with a constant boiling point, is formed, and this mixture may be driven out, leaving a greater part of the alcohol free from water in the lower part of the still. Benzene as well as the alcohol in the ternary mixture may be recovered completely by suitable secondary operations. This is facilitated by the interesting fact that on cooling, the ternary mixture condenses to form two miscible layers, the upper containing most of the benzene, the lower,

most of the alcohol. By means of a separator, these two layers are drawn off and sent to different rectifying stills.

The ternary constant boiling mixture boils at $65^{\circ}\text{C}.$ and consists of

Alcohol	18.5% by weight
Benzene	74.1%
Water	7.4%

It boils considerably lower than pure, dehydrated alcohol ($78.5^{\circ}\text{C}.$).

On condensing, this ternary mixture forms two separate, immiscible layers, which have, at $28^{\circ}\text{C}.$, the following composition:

	Upper layer	Lower layer
Alcohol	11.6% by weight	51.3% by weight
Benzene	85.6%	8.1%
Water	2.8%	40.6%

Of the total, the upper layer is 84.7 per cent, the lower, 15.3 per cent, by weight.

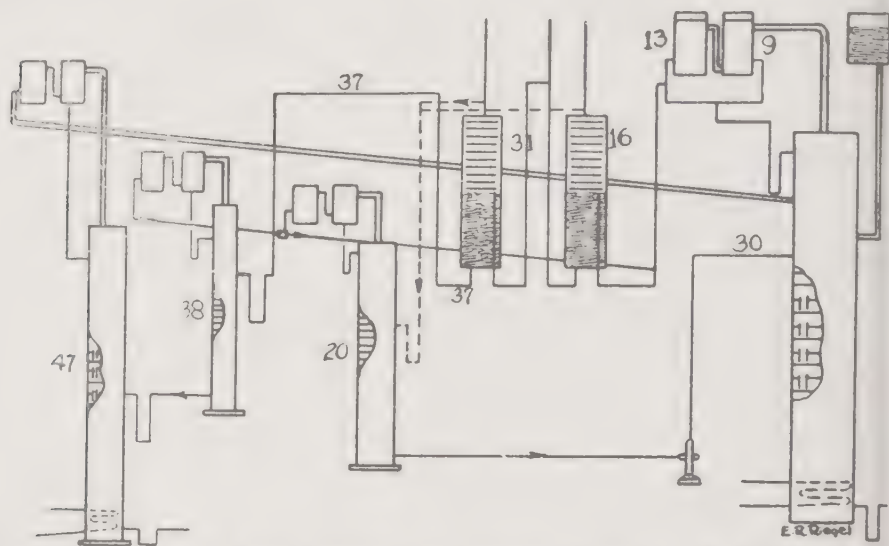


FIGURE 120.—The Keyes process for absolute alcohol. At the right, the main still, giving absolute alcohol at its base. 20, benzene column; 38, alcohol rectifying column; 47, alcohol recovery column. (For other parts, see text.)

The procedure will be described in greater detail, with the aid of Figure 120. Industrial alcohol is fed into a 40-plate still, the main still, at tenth plate from the top. Benzene is introduced, in an amount sufficient to form the constant-boiling mixture with all the water present. Fractionation takes place, the liquid becoming richer in alcohol as it descends while the vapors of the ternary mixture pass out at the top of the still. These vapors reach dephlegmator 9, which is kept at $65^{\circ}\text{C}.$, so that excess alcohol vapor is condensed and runs back to the still; they continue to condenser 13, where they liquefy, and from there run into separator 16, where the two layers form. Heat is supplied to the still by a steam coil; the temperature at the base of the still is $79^{\circ}\text{C}.$ The absolute alcohol is drawn off at that point, cooled and stored.

The upper or benzene layer in 16 passes to the benzene column, 20, and by a steam coil (indirect heat). There rises the ternary constant-boiling mixture, consuming all the alcohol and water, but leaving the excess benzene. This latter is drawn off, cooled, and pumped back into the main through pipe 30.

The lower layer in 16, which might be called the water layer, passes through rubber 31. Water is run in, and two layers form again; the upper layer goes to column 20, where its benzene is abstracted. The lower water layer goes through pipe 37 to column 38, heated again by a closed steam coil. The ternary mixture rises, this time exhausting the benzene, leaving excess alcohol and water in the still. The vapors are dephlegmated and condensed, and pass to 16. From the bottom of 38, a 30 per cent alcohol is drawn and sent to the alcohol recovery column 47, which sends at its top in vapor form 95 per cent alcohol, and allows removal at its bottom of the water. The heat for this column is also indirect. This process has been in successful operation for some years.¹⁹

Other substances instead of benzene may be used as the third constituent in the ternary mixture which is essential to this process; for example, acetate, carbon tetrachloride, or hexane.

Another process which uses a water-immiscible liquid as a means of separating the water from 95 per cent alcohol to produce absolute alcohol is the Steffens process.²⁰

The Glycerin Process. In the process patented by Joseph Van Ruymbeek,²¹ a different principle is applied. A countercurrent of glycerin is used to flow through the still, downward, while the alcohol-water vapor rises. The glycerin acts as dehydrating agent, finally reaching the bottom of the still with all the water combined with it, while the alcohol vapors rising out of the top of the still are low in water, or free from water. Depending on the volume of glycerin relative to the volume of 95 per cent alcohol used. The more the relative amount of glycerin, the drier the alcohol. In order to produce 1000 liters of 98 to 99 per cent alcohol, 1000 liters of glycerin must be fed in at the top of the still.

The glycerin and water passing out at the bottom of the still contain a considerable amount of alcohol. The alcohol is recovered in a second distilling still, in which the glycerin-alcohol-water solution passes down, and steam, injected at the base of the still, passes upward. The alcohol vapors passing out at the top of the still are concentrated in other than the usual way, while a water solution of glycerin is obtained at the bottom. This dilute glycerin is concentrated as explained in Chapter 32, and may then be used over again.

In a later patent,²² the same inventor adds dehydrating salts, such as CaCl_2 , K_2CO_3 , to the glycerin, and obtains alcohol with 99.8 per cent content. The solution of water, glycerin, salts, and alcohol is distilled over steam, as before, and the hydrous glycerin-salt concentrated *in vacuo*.

Although absolute alcohol made by this process is essentially pure, it retains enough benzene to show the absorption bands of benzene, in the ultraviolet region.

U. S. Patent 1,670,053.

U. S. Patent 1,459,699.

U. S. Patent 1,474,216.

at 160° C.; when desired, the glycerin may be recovered by itself by stillation at reduced pressure.

ACETONE AND BUTYL ALCOHOL

Acetone and butyl alcohol are obtained by the bacterial action of selected organisms on corn or other carbohydrate. (See Figs. 121, 122.) In the Fernbach-Strange process,²³ the organism is designated as "of the type of the butylic bacillus of Fitz," and is allowed to act at 30° to 35° C. in the absence of air; 50 per cent of the malted starch is changed, to give acetone and butyl alcohol in the proportions of 1 part acetone to 2 parts of butyl



FIGURE 121.—Butyl alcohol fermentation tanks of 50,000 gallon capacity each; only the top of tank is shown at upper level; the tanks extend through the floor to lower level. (Courtesy of the Commercial Solvents Corporation, Terre Haute, Ind.)

alcohol. In the Delbrueck-Meisenberg process,²⁴ the *Bacillus macran* spread on fruit peel, asbestos, or other inert material with large surface; solution containing the sugar with the necessary nutritive material, the same as for yeast, is added; after 5 days the action is complete; 90 per cent of the sugar (best as molasses) is changed to acetone and butyl alcohol. In the Weizmann process,²⁵ corn is very suitable; the organism is *Bacterium clostridium acetobutylicum*, cultivated from organisms originally found on the surface of the corn and other cereals.

The process is as follows: The crude starch from the corn (Chapter

²³ U. S. Patent 1,044,368 (1912).

²⁴ U. S. Patent 1,169,321 (1916).

²⁵ Brit. Patent 4,845 (1915).

mixed with water in the "mash tuns," then run to the "cookers," closed vessels in which the suspension is heated, giving a thick, sterilized starch paste. After cooling to 98° F. in water-jacketed coils, the starch paste is run to the fermenting tanks; a charge of bacteria culture is added, 800 gallons of culture to 40,000 gallons of paste. The action begins after four hours; the jelly-like starch paste begins to liquefy, gradually becoming a watery liquid. At the same time, gases are evolved and pass out with great violence. Gradually the foaming subsides, and 48 hours after the addition of bacteria to the paste, the action is over. The starch has been converted into liquid products and gases (hydrogen and carbon dioxide).

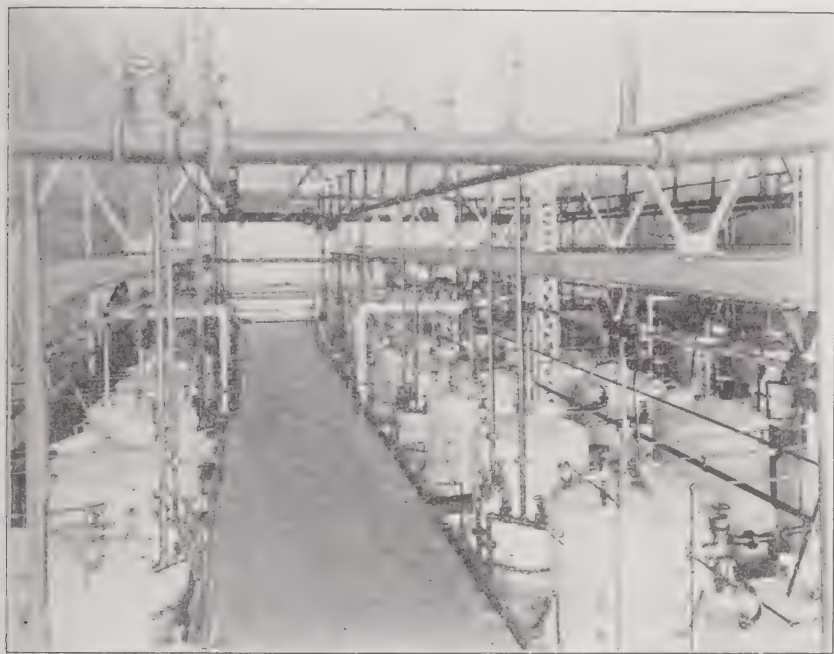


FIGURE 122.—800-gallon bacteria-propagation tanks for butyl alcohol fermentation; one tank furnishes the right amount of culture for one 50,000-gallon fermentation tank. (Courtesy of the Commercial Solvents Corporation, Terre Haute, Ind.)

liquid products are formed in the ratio of 6 parts butyl alcohol, $\text{C}_4\text{H}_9\text{OH}$, 3 parts acetone, and 1 part ethyl alcohol.

Extreme care is used to protect the *Clostridium acetobutylicum* from outside influences which might decrease its activity. A supply of the pure organism is always at hand, and more put away, mixed with dry, sterilized starch, in which condition it lies dormant for months and even years. A little sterile earth is placed with an ounce of starch paste in a test-tube, kept at 98° F.; after one day, it is liquid, and the ounce is placed in a quart of the same. In one day, this is liquid, and is placed in a 10-quart flask; at one day's interval, transfer is made successively to an 80-quart lot in an enamel vat, then to the final 800-quart batch. Each fermenting vat receives a

culture made directly from the dry earth bacteria, over a period of days.²⁶

The purification consists of the following steps: The product of bacterial action, called the "beer," is distilled in order to separate all the volatile substances from the non-fermented residue. The distillate is next separated by a second distillation into the acetone fraction (boiling point 56° to 132.8° F.), the ethyl alcohol fraction and the butyl alcohol fraction. These three are refined further; the refining of the last is done in accordance with an interesting patent.²⁷

The hydrous butyl alcohol is distilled in a column still with plates, heated by a steam coil; as received from the previous distillation, it contains water. There passes over a constant-boiling mixture containing 70 per cent butyl alcohol and 30 per cent water, at 90° C. (194° F.); on cooling, this distillate separates into 2 layers, an upper layer with 20 per cent water and 80 per cent butyl alcohol, and a lower layer with 96 per cent water and 4 per cent butyl alcohol. The lower layer is drawn off and sent through the stills again; the upper layer is returned to the still, where it forms once more the 30 per cent constant-boiling mixture, which passes out. The vapors passing out carry more water than the liquid returned, so that the still gains in butyl alcohol, and loses in water. Some excess alcohol vapor passes out with the constant-boiling mixture, but is returned to the still by a dephlegmator kept at 95° C. (203° F.), which condenses it (boiling point 117° C., 242.6° F.), while it allows the 70 per cent mixture to pass to the cold condenser. Finally the still contains only anhydrous butyl alcohol; this condenses on the upper three plates, free from any impurities and may be drawn off from there.

Butyl alcohol itself is a solvent in lacquers; besides, it serves to make butyl acetate, a still more valuable and important solvent (see table of chemical manufactures), and a number of other esters. Butyl alcohol is manufactured not only by fermentation, but also by synthetic processes.

In 1935, 58,145,494 pounds of butyl alcohol, by fermentation and synthesis, were produced (9 cents a pound).

The hydrogen and carbon dioxide gases from the fermentation tanks are utilized in the catalytic synthesis of methanol, one of the most brilliant achievements in chemical technology (Chapter 25).

During the first World War, both acetone and ethyl alcohol were greatly needed, while the demand for butyl alcohol was limited. Efforts were made to develop an organism which would produce acetone and ethyl alcohol or one such investigation resulted in the culture of a new organism, which is called *Bacillus acetoethylicum*.²⁸

Synthetic amyl alcohol, to which reference has already been made in this chapter, is obtained by chlorinating pentane, a low-boiling fraction (boiling to 37° C. or 84° to 96° F.) of casing-head gasoline.²⁹ The chloropentane is then hydrolyzed, giving normal amyl alcohol; amyl alcohol from it

²⁶ From a description kindly furnished by the Commercial Solvents Corp., Terre Haute, Ind.

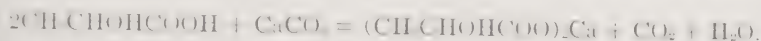
²⁷ U. S. Patent 1,394,232 (1921).

²⁸ *Ind. Eng. Chem.*, **11**, 723 (1919); or U. S. Patent 1,293,172.

²⁹ "High-boiling solvents from natural gas pentanes," Lee H. Clark, *Ind. Eng. Chem.*, **22**, 439 (1930).

is a mixture of iso-amyl alcohol and optically active (dextro) amyl alcohol.

Lactic Acid. Lactic acid is formed by the action of *Bacterium lactis* on molasses or other sugar-containing material. After dilution, chalk added, and a nutritive solution, and the action allowed to take place at 45° C. (104° to 113° F.); the chalk is acted on by the lactic acid as it is formed, and carbon dioxide given off:



The chalk must be added because the bacteria become inactive if the concentration of the acid is allowed to rise above 1 per cent. The calcium lactate precipitates and is filtered, washed, and treated with dilute sulfuric acid which liberates the lactic acid in solution form. The calcium sulfate is filtered off, the solution of lactic acid clarified, and concentrated to 50 per cent lactic acid, a thick solution. Pure racemic lactic acid melts at 18° C. The 50 per cent solution is used in textile plants, and, especially purified, in certain foods.

The souring of milk is due to the same organism, which forms lactic acid from the sugar in the milk, the lactose.

Citric Acid. Citric acid is made from cane sugar by the action of *Aspergillus niger citrius*. The culture is added to a 10 to 12 per cent sugar solution, containing also a suitable nutrient solution, in flat, open tin pans, at about 40° C. (104° F.). Precautions are taken to keep various batches from contamination by foreign bacteria. The raw liquor is worked up by adding milk of lime; the citric acid later is regenerated by means of sulfuric acid. The acid liquor is purified by adding sodium ferrocyanide solution, to precipitate any copper and iron, and is then concentrated in lead-lined steel evaporators. The strong liquor is crystallized, at rest, to form large transparent crystals, or with agitation, to form granular citric acid, in either case, $\text{C}_3\text{H}_4(\text{OH})(\text{COOH})_3 \cdot \text{H}_2\text{O}$. The anhydrous acid is in even greater demand than the crystals; opaque anhydrous citric acid is made directly from a hot solution by crystallizing at 40° to 100° C. under a high vacuum (730 mm.).³⁰ Natural citric acid is made from the juice of lemons, in Italy and California.

The manufacture of glycerin by fermentation is included in Chapter 32. The commercial importance of a number of substances mentioned in this chapter is indicated by the dollar figures in the Table of Manufactures, at the beginning of the book. For citric acid, the 1935 production was 10,493,000 pounds, at 27.4 cents a pound.

VINEGAR

A dilute alcohol solution seeded with *Bacterium aceti*, after the addition of a nutritive solution, causes the formation of acetic acid, provided air has access to the vat. The reaction is:



Wines are used to make vinegars, and furnish the strongest (8 per cent acetic acid) as well as those with the best flavor. Cider which has been fermented is largely used, and furnishes a 4 to 5 per cent vinegar.

The *Bacteria aceti* form films which are called mother of vinegar; souring may take place in casks, the new stock being seeded by leaving a portion of the finished vinegar to mix with it. The more general process is to pour the new stock down shavings which carry the mothers, while a gentle current of air passes upward.

A very fair amount of acetic acid made by bacterial action is used in the chemical industries, as such, and for the manufacture of ethyl and other acetates; generally the dilute acetic acid may be used.

Ethyl alcohol may be changed into acetic acid by catalytic oxidation at elevated temperatures.

OTHER PATENTS

U. S. Patent 1,885,096, process for producing butyl alcohol, acetone, and ethyl alcohol from the same mash; 1,858,808, butyl alcohol and acetone from a mash of waste pulp of a potato flour factory; 1,858,488, propagating yeast in a yeast nutrient solution consisting of a water solution of molasses, urea and in non-ammoniacal inorganic yeast nutrient solutions; 1,766,715, production of lactic acid and its derivatives by fermentation of materials containing carbohydrates; 1,875,536, continuous fermentation process for the production of butyl alcohol; 1,802,163, manufacture of butyl alcohol by fermenting a mash consisting of molasses, a phosphate, and an addition of malt germ; 1,818,530, continuous manufacture of yeast by the air-fermentation method; 1,380,000 and 1,432,761, chlorine on pentane in presence of activated charcoal and esterification of the amyl chloride at 400° to 450° F. and 250 lbs. pressure; 1,982,160, manufacture of acetic acid from alcohol; U. S. Patent 2,230,318, alcohol production by fermentation; British Patent 523,262 on using bran and cereal germs.

PROBLEMS

1. A Cuban molasses has a specific gravity of 1.4, and the analysis given in the text. There are received 100,000 gallons at Baltimore, brought by tankers; this amount is fermented for ethyl alcohol. The conversion is 90 per cent, and the recovery of the alcohol in the beer in the form of industrial alcohol, 94 per cent. Express in pounds of 100 per cent alcohol, how many pounds are collected? If the industrial alcohol is 95 per cent, how many gallons are obtained, the specific gravity being 0.8?

2. The starch contained in one ton of dry corn, with 73 per cent starch, is separated and cooked into a paste. It is then fermented to butyl alcohol and accompanying products as listed in the text. The liquid products are, let us assume, 50 per cent by weight of the starch taken. How many pounds of each are obtained? The partition the several products are parts by weight.

3. Citric acid anhydrous is made from cane sugar; the acid made is 75 per cent by weight of the sugar taken. Over a period of several days, 10 tons of cane sugar are fermented into opaque anhydrous citric acid. The yield in crystal from acidulated the hot liquor is 80 per cent. Find the weight of product.

4. A brewery plans to produce 100 barrels of beer a day. How many fermentation tanks will be required, how many mash tuns and copper boilers? In order to have proper capacity, what will be the size and number of the various vessels? Let the fermenting vats be square in cross-section, the other vessels circular. It may be assumed that 105 barrels of wort will be required for the intended production.

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In a democracy, it is necessary to disseminate news readily and cheaply. One of the indispensable agencies in that process is an abundant supply of paper. For the transfer of knowledge from generation to generation, and for the preservation of knowledge, paper is required. This material is therefore not only a convenience, but one of the cornerstones of our civilization.

Chapter 21

Cellulose from Wood; Pulp and Paper*

The importance of the pulp and paper industry in the field of industrial chemistry can be comprehended from the single statement that the per capita consumption of paper in the United States within recent years approximated 250 pounds per year.

An idea of the rate of development of the industry can be obtained by contrasting this per capita requirement with that for several selected years. Because, for the most part, with perhaps the exception of newsprint production, facilities for papermaking in the United States have increased only slightly more rapidly than consumption. Newsprint capacity, on the other hand, has fallen far behind requirements as developed during the past quarter century. The annual per capita paper consumption figures for selected years follow:

Year	Pounds Consumed per Capita
1810	1
1819	2
1869	20
1899	57
1914	112
1929	220

The invested capital in the pulp and paper industry of the United States is estimated at approximately one and one-half billion dollars. This capital structure, according to figures for 1942, is spread over 531 firms which operate 253 pulp mills and 745 paper mills. The pulp mills are distributed over 26 states; the paper mills over 37 states and the District of Columbia. Most of the pulp mills are integrated with paper mills; a few are not. Some

TABLE 43.—*Estimated annual consumption of chemical raw materials by U. S. pulp and paper industry.*¹

Raw Material	Quantity in Short Tons	Raw Material	Quantity in Short Tons
Lime	344,500	Alum	117,500
Silicate of soda	283,600	Rosin	88,000
Salt cake	225,000	Soda ash	80,000
Sulphur	204,000	Caustic soda	40,000
Limestone	188,090	Casein	18,000
Chlorine	146,000		

of the pulp mills not integrated with paper mills are owned by paper organizations and serve as sources of pulp supply for paper mills operated by them. Sometimes more than one kind of pulp mill is combined with a paper mill into a single operation. Newsprint, for example, usually is made

* Prepared especially for this edition by Mr. Harry E. Weston, Editorial Director, *Paper Industry and Paper World*.

¹ From estimates presented in the September, 1937, issue of *Chemical and Metallurgical Engineering*.

mill which also produces sulfite pulp and groundwood pulp, these two kinds of pulp being commonly combined to make newsprint. Based on tonnage, Washington, Maine, Louisiana, Wisconsin, and Florida, in the order given, were the five most important pulp producing states in 1940. If the rating is on value of pulp rather than tonnage, the order would be Washington, Maine, Wisconsin, Louisiana, and New York. New York, Michigan, Maine, Wisconsin, and Ohio, in the order given, were the states of greatest paper tonnage during 1940.



FIGURE 123.—Pulpwood in storage in mill yard. (Courtesy of Jeffrey Mfg. Co.)

To produce these tremendous tonnages of pulp and paper requires numerous raw materials. For purpose of easy classification, these materials may be broadly divided into two groups, namely, fibrous and non-fibrous. The important fibrous raw materials are wood, waste paper, cotton and rags—both old and new—straw, old rope, and cotton linters; the non-fibrous are lime, silicate of soda, salt cake, sulfur, limestone, chlorine, clay, rosin, soda ash, and caustic soda.

Published statistical data reveal that the following wood species, in the order given, accounted for nearly 90 per cent of the quantity of pulpwood consumed by United States mills in 1940: southern yellow pine, spruce, hemlock, poplar, jack pine, and balsam fir. The total consumption of pulpwood in 1940 by these same mills amounted to 13,742,958 cords. Of the total consumption, about 10 per cent, much of which was spruce, was imported. For the most part, this huge quantity of wood is reduced to pulp by one of four processes, a fifth process being employed to a more limited extent. The four major pulping processes are designated as groundwood

TABLE 44.—*U. S. pulpwood consumption (1940).*

Species	Cords	Species	Cords
Southern yellow pine....	5,013,478	Beech, birch and maple ²	298,89
Spruce ¹	3,008,714	White fir ¹	213,43
Hemlock ¹	2,788,771	Cottonwood	74,58
Poplar ¹	598,675	Tamarack (larch)	11,32
Jack pine ¹	477,975	Other woods ²	509,97
Balsam fir ¹	472,186	Slabs and mill waste ...	274,93
		U. S. total	13,742,99

¹ Domestic and imported.² Chestnut, Douglas fir, yellow poplar, oak, tupelo (and black gum), red gum, willow, and lanaceous hardwoods.

or mechanical, sulfite, soda, and sulfate; the fifth process, as semi-chemical. The groundwood or mechanical pulp process, as its name indicates, is strictly mechanical in character; the sulfite, soda, sulfate, and semi-chemical processes are chemical in nature; the sulfite process employs an acid liquor for pulping; the soda process, an alkaline liquor; the sulfate process, an alkaline liquor; and the semi-chemical process, a neutral liquor.

TABLE 45.—*U. S. wood pulp production by kinds (1940).*

Kind	Quantity in Short Tons	Kind	Quantity in Short Tons
Mechanical	1,762,821	Semichemical and other	
Sulfite	2,591,684	wood pulp	164,948
Sulfate	3,725,135	Screenings (mechanical	
Soda	548,047	and chemical)	59,113
		U. S. total	8,851,744

Wood Preparation. To convert wood into pulp by any of the pulp-making processes, it first is necessary to remove its bark, and, in the case of chemical pulp, to reduce the barked wood into small chips of fairly uniform size. The nature of the operations for doing this work depends somewhat on the relative sizes of the wood being pulped, the method or methods employed in getting the wood to the mill, and the kind and quality of the wood that is being produced by the mill.

Although there are a number of different designs of machines employed for removing bark from pulpwood, probably the barking drum is the most common of them. This machine consists of a cylinder-like drum or a combination of drums, sometimes as much as 12 feet in diameter and 45 feet long, positioned horizontally, that is, they are made of special-shaped, longitudinally placed steel sections, individually spaced to permit the bark of the wood to pass between them. In operation, this drum is revolved slowly, only a few revolutions per minute; the wood, cut to a uniform length (commonly not exceeding five feet), enters continuously at one end, tumbles around within the drum, and discharging from it continuously at the other end, the bark being removed by the tumbling of the various short sections of wood against one another in their passage through the drum. Water also is used in the operation to free the barked wood of any loose bark that otherwise might adhere to it.

The capacity of equipment of this kind is influenced largely by the species of wood being barked and by the condition of the wood at the time of barking. A barking drum with a diameter of 10 feet and a length of 30 feet, for example, might handle four to five cords of dry, frozen soft

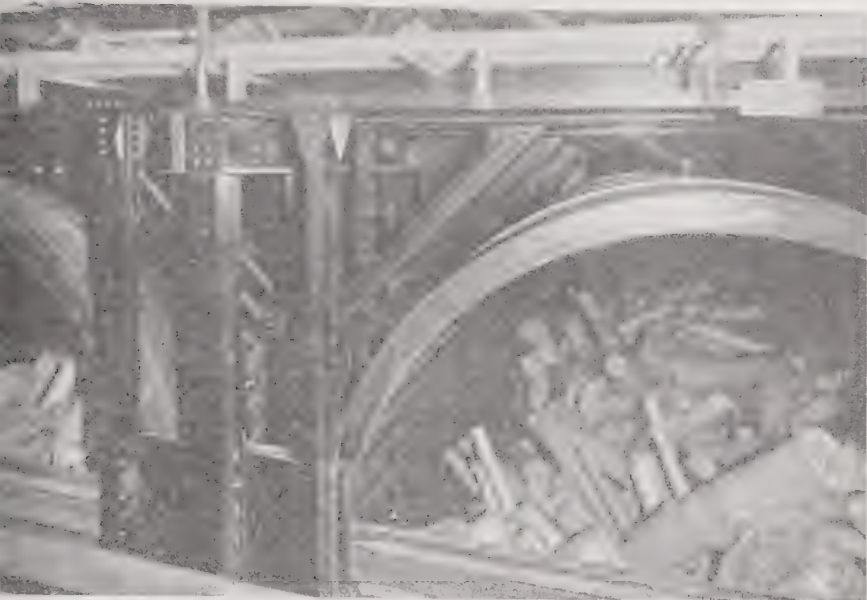


FIGURE 124.—Wood being barked by two barking drums. (Courtesy of Chicago Bridge & Iron Co.)

wood per hour, as contrasted with 10 to 20 cords per hour if the wood is hand-driven.

The barked wood, without any further preliminary treatment, is ready for direct use in the production of mechanical pulp. To make it ready for treatment by any of the chemical pulp-making processes, however, it must be further reduced to chips, which approximate from one-half to one inch in length and from one-eighth to three-sixteenths of an inch thick.

The chipping is accomplished in a machine known as a chipper, which cuts the wood, as it passes through the machine lengthwise, a slicing cut at an angle of about 45 degrees. This type of cut allows the natural pores of the wood to remain open and at the same time presents a much greater surface area to the action of the pulping chemicals, penetration taking place mainly through the ends rather than on the flat side of the chips.

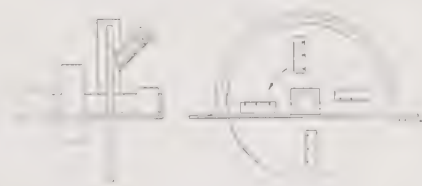


FIGURE 125.—Wood chipper.

The chipper consists essentially of a hooded, heavy circular disc, made of cast-iron or heavy steel plate, slotted for and equipped with three or more knives (as many as 8 or 10 on some of the newer units), positioned vertically on a horizontal shaft, together with a cast-iron hopper so placed in relation to the face of the disc that it directs the wood

against it and to the cutting edge of the knives at the proper cutting. A common size of four-knife chipper has a disc 84 inches in diameter and a capacity of about 10 cords per hour. The largest wood chipper ever so far as is known, has a disc 171 inches in diameter. Installed in a L Coast mill during 1941, this chipper is designed for handling wood 40 inches in diameter, has a rated capacity of about 145 cords per hour and is equipped with a 1000 hp. motor.

Practical uniformity in chip size is important in the successful digesting or cooking of the wood. Therefore, the chips produced by the chipper are screened to separate those of desirable size from oversize material and dust. The oversize material is crushed or reduced in size and re-screened. The sawdust is frequently utilized for fuel.

Several designs of chip screens are in common use. They include types as revolving or rotary, shaker or reciprocating, vibrating, and oscillating. The revolving screen commonly consists of a single or double cylinder arrangement, the screening surface depending upon the design; although the shaker, vibrating and oscillating units may vary somewhat in design. The primary difference of the several designs is in the method of imparting screening action to the tables.

Liquor Preparation. Roughly speaking, about 2,000 gallons of cooking liquor are required per ton of chemical pulp. This requirement necessitates an extensive layout of equipment for use in producing such liquor in a sulfite, soda, and sulfate mill. In the case of the sulfite mill, the equipment is grouped together in a portion of the mill designated as the acid plant. In the case of the soda or sulfate mill, the combination of equipment for liquor preparation in a soda or a sulfate mill is known as the chemical recovery plant.

Sulfur (or a source of sulfur such as iron pyrites), limestone or lime, and water are the chemical raw materials needed in the preparation of cooking liquor. The sulfur is burned, or the pyrites roasted, to produce sulfur dioxide gas. Since sulfur is so readily available to United States mills, it is the common raw material used for producing the gas. In burning the sulfur, it is necessary to control both the temperature of burning and the quantity of air supplied for it. The usual temperature range for the gas, just previous to being cooled, the next operation in the cycle, probably is from 700-1000° C. Theoretically, one pound of oxygen, the quantity contained in about 54 cubic feet of air, is required to convert one pound of sulfur into two pounds of sulfur dioxide gas. Somewhat more air than the theoretical amount is required in practice.

Cooling of the gas is essential to its absorption in water. Rapid cooling is necessary to minimize the production of sulfur trioxide. Absorption of the gas in water is carried out in the presence of lime (as milk-of-lime) or of limestone. In either case, the result is the same, namely: a bisulfite liquor containing an excess of sulfurous acid. To this liquor, which is designated as raw acid, is added sulfur dioxide gas relieved from the digester during the cooking cycle to obtain the cooking acid of the process.

In brief, therefore, the major equipment of an acid plant used to produce cooking acid for a sulfite mill would include one or more sulfur burners and a combustion chamber arrangement, a gas cooler (water being used

coolant, absorption apparatus, and equipment to permit the use of hot gas for strengthening of the raw acid. In the latter case, the gas and the raw acid may be brought together in an accumulator, a recent but widely accepted development which makes possible the use of a hot and stronger acid in charging a digester; or it may include a gas washer (also using water as a coolant) and a recovery tower.

Sodium carbonate, lime and water are the raw materials commonly used in the production of the cooking liquor of the soda process. This liquor is usually a solution of caustic soda, with a strength of 8° to 15° Bé. at 60° F. It is made by causticizing a solution of soda ash with quick lime. The causticizing reaction produces not only the caustic liquor but also a precipitate of calcium carbonate. This precipitate is settled out or filtered from the caustic liquor. By far the larger part of the soda ash required for the process, from 80 to 85 per cent, is obtained from cooking liquor which has previously been employed for pulping. Only enough replacement soda ash has to be used to make up for losses which occur in the cycle of mill operations.



FIGURE 126.—General view of modern pulp and paper mill. (Courtesy of Chicago Bridge & Iron Co.)

The liquor of a digester charge following cooking, designated as black liquor, is obtained for alkali recovery through the pulp washing operation, an operation essential in the making of soda pulp fiber suitable for use in paper making. This liquor, diluted tremendously by the washing operation, contains nearly all of the alkali of the original liquor, but also contains about half the weight of the wood of the digester charge. It is common practice in making this alkali available for reuse to first concentrate the liquor to about 35° Bé. and then to pass it through an incinerator from which it is discharged as a very hot cinder, known as black ash, and consisting largely of a mixture of sodium carbonate and carbon. Constituting about 65 to 80 per cent of the weight of the black ash, the sodium carbonate is leached free of the carbon, thus making it available for causticizing with lime.

The chemical recovery plant of a soda pulp mill, therefore, consists essentially of an evaporator and incinerator installation for making the alkali in the black liquor available for re-use as sodium carbonate, an installation including tanks to free the sodium carbonate in the black ash from the

carbon also contained in it, and a causticizing plant to convert the sodium carbonate into caustic soda.

The raw materials used in the production of sulfate cooking liquor are sodium sulfate, lime, and water. In the preparation of this liquor, like that of the soda process, use is made of the cooking liquor from previous pulp operations. This liquor, also designated as black liquor just as in the soda process, likewise is concentrated by evaporation following the pulp-washing operation. The concentrated liquor then may be handled in one of two ways. The older process involves the formation of black ash as in the soda process, mixing this ash with the quantity of sodium sulfate necessary to make up for the loss of alkali, feeding this mixture into a smelting furnace (the carbon in the ash serving as a source of fuel), where the sodium carbonate is reduced to sodium sulfide and the sodium carbonate of the ash is freed of the carbon by the burning operation, and then causticizing with lime the smelt that issues from the furnace, thus producing a cooking liquor consisting largely of caustic soda and sodium sulfide, and a precipitate of calcium carbonate. The newer method, in part, involves mixing the sodium sulfate with concentrated black liquor, and feeding this mixture into a chemical recovery unit, which combines a smelting furnace and a steam boiler. Here, the carbon of the liquor serving as the source of fuel for the sodium sulfate is reduced to sodium sulfide, and the steam is produced for power and process use. The smelt issuing from such a unit, as in the case of the older smelting furnace, consists essentially of a similar mixture of sodium carbonate and sodium sulfide, which when causticized produces the cooking liquor of the process and a precipitate of calcium carbonate. This calcium carbonate precipitate, commonly designated as lime sludge, may be calcined and the lime so produced used in part as a source of lime for causticizing.

Therefore, equipment essential to the production of sulfate cooking liquor would include an evaporator installation, and, depending upon the method of sodium sulfate reduction, a rotary incinerator and smelting furnace combination, or a chemical recovery unit with steam boiler and steam engine, together with necessary equipment for causticizing and possibly a kiln for calcining the sludge.

The semi-chemical process does not delignify the wood to the extent of any of the previously mentioned chemical processes. It merely softens the chips, which are then reduced to pulp mechanically. Pulp yields by the semi-chemical process, which commonly employs a neutral sodium sulfite liquor for cooking, ranges from 70 to 80 per cent of the weight of the wood. One of the uses of the process is in the utilization of tannin—extracted chestnut bark—in the production of stock for corrugating board.

Pulping Wood Mechanically. A machine designated as a grinder is used to reduce the barked wood to mechanical pulp. Within recent years, considerable development in grinder design has taken place; so that the grinders now in use may be classified broadly into one of three types—pocket-magazine, and pocket-magazine combination. Whatever the design, the grinder includes a cylinder-like pulpstone (either natural or manufactured) positioned on a horizontal shaft and a means for forcing the barked

st its face during operation. The wood always is placed lengthwise as the pulpstone face, so that as the stone revolves, the wood fibers are cut from one another in their lengthwise direction. Sufficient water is added in the grinding operation, both to prevent burning of the wood and to serve as a vehicle for carrying the pulp fiber away from the machine.

In the case of the pocket grinder, wood is fed intermittently into one or several chambers or pockets, located radially along the upper half of the periphery of the pulpstone, and there forced against the pulpstone face by means of a hydraulically operated piston arrangement. The older type of magazine grinder makes use of two vertically positioned, wood-charging

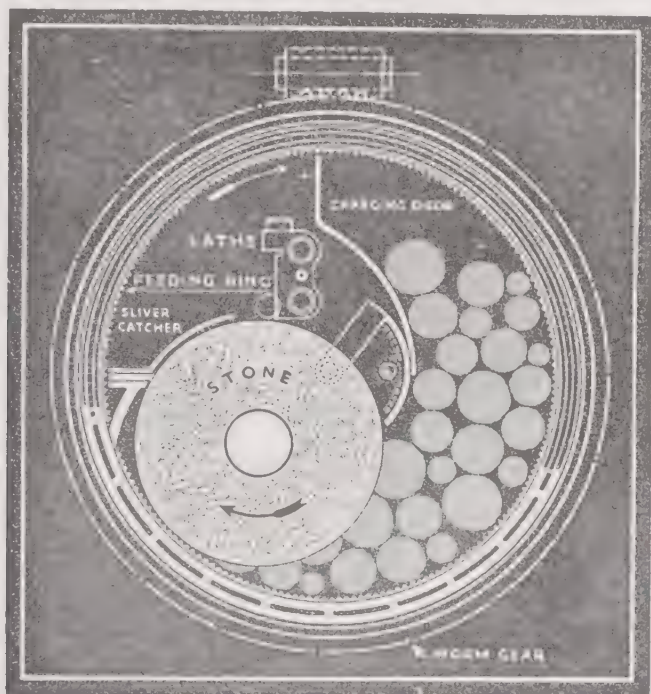


FIGURE 127—Elevation Sketch of a Recently Developed Woodpulp Grinder Showing Principles of Operation. (Courtesy of The Appleton Machine Co.)

magazines in relation to the pulpstone and an intermittently and automatically—operated pocket-type feeding arrangement for each magazine. This design was followed by a single vertically positioned magazine directly against the pulpstone, so designed as to force the wood continuously against the stone. The most recently developed magazine grinder employs a large iron ring so mounted eccentrically around the pulpstone and within an iron housing that the ring almost contacts the stone at a point about 45° from the vertical. Such a positioning of the stone in relation to the ring leaves a relatively small space on one side of the stone and a large crescent-shaped area on the other side. A baffle, built into the smaller area, functions as a sliver pocket; the crescent-shaped space, also utilizing a

baffle arrangement, serves as the loading pocket for the wood. With rotation of both the ring and the stone, both in the same direction, the stone at a constant speed of approximately 240 rpm., the ring at a speed varied to the operating pressure desired, a charge of wood, usually a one-half cord, is reduced to pulp.

TABLE 46.—U. S. wood pulp production by States (1940).

	Short Tons		Short tons
Washington	1,443,121	Minnesota	247,077
Maine	1,080,818	Alabama	246,960
Louisiana	864,552	Pennsylvania	231,533
Wisconsin	729,615	Michigan	212,853
Florida	583,294	Vermont	19,133
New York	526,367	Other Southern States ¹ ..	1,076,977
Virginia	496,918	Other Northeastern and	
Oregon	396,142	Central States ²	402,244
North Carolina	294,130		
		U. S. total	8,851,744

¹ Arkansas, Georgia, Mississippi, South Carolina, Texas.
² Maryland, Massachusetts, New Hampshire, Ohio, Tennessee.

The pocket-magazine combination type of grinder makes use of two pockets and two magazines. Each pocket, one on either side of the grinding surface, positioned somewhat nearer the horizontal than in the older type of pocket grinders, carries a magazine in its top to permit ready charging with wood.

Among the more important operating factors to be considered in the grinding of wood for mechanical pulp are: condition of pulpstone surface, speed of stone, operating pressure, temperature of grinding, and the physical condition and species of wood being ground.



FIGURE 128.—Digester for sulfite pulp.

Chemical Reduction of Wood to Fiber. Digesters used for cooking wood chips with acid or alkali are usually vertically-positioned cylindrical pressure vessels of steel plate construction. The sulfite digester common

er than either the soda or sulfate digester. It also is lined with acid-resisting brick while no lining is required for digesters used in alkaline pulping. A sulfite digester with a diameter of 15 feet, a height of 50 feet, and walls 10 inches thick will hold approximately 22 cords of wood per charge. The yield of fiber from a digester charge is dependent upon a number of factors. Among the more important of these factors would be the specific gravity or density of the wood, the strength of the cooking liquor, the temperature and pressure of the cooking cycle, and the time interval or length of cycle.

In general, it will average a little less than 50 per cent. Although in some instances steam is introduced directly into a digester, modern practice favors external heating and forced circulation of cooking liquor. When a forced circulation system is employed, the digester may be heated indirectly through the use of a heat exchanger or directly through the incorporation of a special type of heating unit into the circulating system.



FIGURE 129.—Operating floor in digester house of sulfate pulp mill.
(Courtesy of *Paper Industry and Paper World*.)

There is no standard procedure for the handling of a digester charge. The procedure varies with the individual mill. Probably a typical sulfite cooking procedure for an easy bleaching pulp would be somewhat as follows: (1) bring digester to cooking pressure of 75 pounds in two hours; (2) increase digester temperature gradually to about 150°C . (302°F .). Maintain pressure at 75 pounds by relieving gas pressure on charge. Time interval about 10 hours from initial steaming; (3) shut off steam supply. Con-

time relieving for one hour to bring pressure down to 50 pounds; (4) charge digester contents at 50 pounds pressure.

It is common practice in both soda and sulfate cooking procedures to reach cooking pressure as soon as possible and to maintain the charge at this pressure to the end of the cook. Likewise, higher operating pressures and shorter cooking cycles are used than in sulfite. Usual practice calls for a pressure of 100-110 pounds and a cooking cycle of three to six hours.

Washing Chemical Pulp. With the cooking operation completed, the digester contents are discharged under pressure into a specially designed tank which permits rapid removal of the blow steam to the atmosphere, or, in the case of some of the newer sulfate mills, to a condenser. If a direct down condenser is used, it furnishes hot water for use in pulp washing, the next immediate operation to follow.

The tank used for receiving the digester charge and for pulp washing in a sulfite mill is designated as a blowpit. It is commonly of wood construction, making use of a vertical stack for removal of blow steam to the atmosphere and a false bottom for washing the pulp free of the spent liquor of the operation.

This liquor, commonly designated as waste sulfite liquor, has attracted the attention of numerous research workers. Commonly, it is discharged into the stream or other body of water upon which a mill is located, and as a result, pollution of the water has become an acute problem in a number of sulfite mill communities. Up to the present, most mills do not utilize this liquor in any way because of their inability to do it economically. However, in few instances, it is being used as a road binder, tanning material, and as a source of fuel, as well as in the production of vanillin, pigments, yeasts, and other products.

In a soda or sulfate mill, a tank, known as a cyclone or blow tank, may be used to receive the digester charge and to exhaust the blow steam from the pulp stock and black liquor of the charge being discharged from it by gravity, as desired, into one of a series of wash tanks or pits; or the charge may be blown directly into one of a series of tanks, known as diffusers, which serves in the same way as the blowpit of the sulfite mill.

Screening the Pulp Fiber. After the washing operation is completed, large quantities of water being used for the purpose, the chemical pulp is ready for screening. A similar screening procedure is required of groundwood pulp as it issues from the grinder; but, in producing groundwood pulp, no washing operation, as practiced in making chemical pulp, is required. The purpose of the screening operation is twofold: first, to remove slivers and small unground slabs from groundwood pulp as it issues from the grinder pit, and to remove knots and other partially cooked chips from the washed chemical pulp; and secondly, to separate the main mass of pulp into two or more grades depending primarily upon variation in diameter. The screening procedure, therefore, is commonly divided into two operations—coarse screening and fine screening.

Coarse screening of groundwood pulp is accomplished by the use of a machine called a sliver screen; the machine employed for the coarse screening of chemical pulp fiber is known as a knotter. There are a number

rent designs of machines for performing this coarse screening operation. In some instances, the machine is designed to handle either groundwood or chemical pulp; in other instances, just one or the other. One design of the screen, adapted to either groundwood or chemical pulp fiber, with screening cylinder 5 feet in diameter and 12 feet long and with $\frac{3}{16}$ -inch perforations in the screen plates constituting the cylinder, has a capacity of 100 tons of mechanical pulp or 50 tons of chemical pulp per 24 hours. The same machine with $\frac{1}{4}$ -inch perforations in the screen plates can handle 125 tons of mechanical pulp or 65 tons of chemical pulp per 24 hours.

In this machine, the slivers and screenings, also called tailings, are freed of fibers as they travel from the inlet end of the screen to the tailings discharge at the opposite end. A spiral within the screening cylinder retards movement of the slivers and screenings in their passage through the machine and forces them to travel nearly 100 feet before being discharged. Accepted fiber, on the other hand, passes through the screen plate perforations into a pit or vat from which it is delivered to the fine screen installation.

In general, fine screens may be classified into one or two types, either diaphragm (flat), or centrifugal. The diaphragm or flat screen depends its operation upon both gravity flow and suction or vibration; centrifugal force is utilized in the operation of a centrifugal screen.

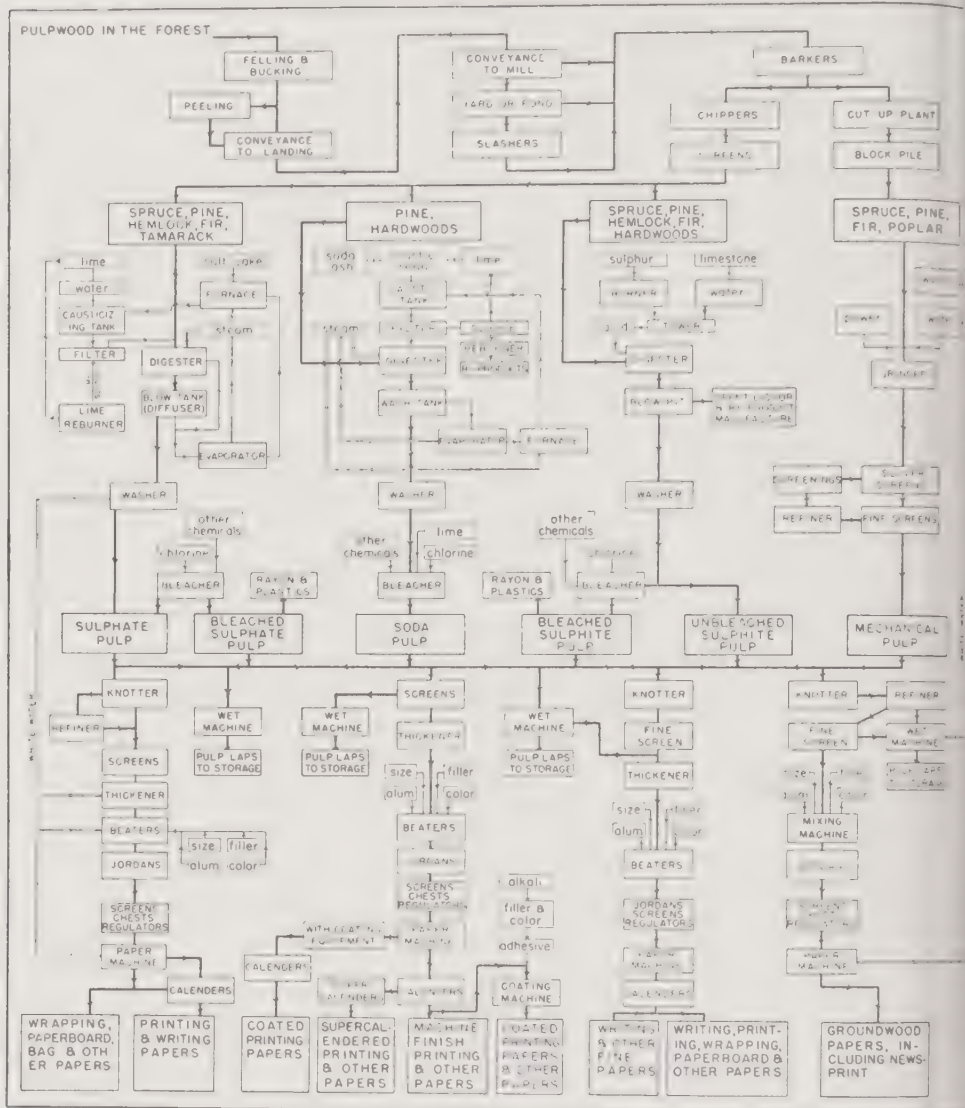
The diaphragm screen is characterized by a series of slotted metal plates positioned near the bottom of a comparatively shallow box or vat of wood or metal construction; below this, forming the bottom of the vat, are a series of diaphragms, which, when actuated, serve to draw the accepted stock through the slots in the plates. The width of slots in a given plate is dependent upon the kind of pulp being screened and upon the kind of equipment required of the screen installation. A modern 12-plate screen, with plates 12 by 43 inches, will have a capacity of approximately 6 to 11 tons of pulp fiber per 24 hours.

The centrifugal screen consists of an impeller surrounded by an assembly of screen plates which in turn is surrounded by the machine casing. Positioned either horizontally or vertically, the impeller, when in operation, forces the stock being screened against the screen plates, the accepted stock passing through the perforations in the plates to the area within the casing; from this it is discharged, the tailings passing from within the screen plate assembly to a secondary or tailings screen for a final separation of acceptable stock from the rejects. The perforated openings in the screen plates, dependent upon the make of screen and the service, usually range from .055 to .01 inch diameter.

Both diaphragm and centrifugal screens are designed for continuous operation on a very dilute suspension of fibers. Screened stock generally has a consistency of only .25 to .60 per cent.

De-Watering or Thickening the Stock. Because of the low consistency of screened stock, a de-watering or thickening operation must follow screening. This operation is necessary whether the pulp is to be used immediately in the succeeding operations or whether it is to be stored or shipped. The

desired concentration of pulp fibers determines the type of machine employed for thickening. If a consistency of only 3 to 6 per cent is desired the machine may consist of a vat for receiving the screened stock; a revolving cylinder, with a wire cloth facing, which is suspended in the vat



This diagrammatic chart does not represent a typical mill layout, it is, rather, a composite of several types of manufacture

FIGURE 130.—Diagrammatic chart of materials and equipment used in the manufacture of wood pulp and paper. (Courtesy of the American Paper and Pulp Association, 122 East 42 street, New York.)

some means for removing the fiber mat which forms over the facing of the cylinder as it revolves in the stock. Such a machine commonly called a deeker. If a consistency of 15 to 25 per cent or more is desired vacuum filter, such as is common to the chemical industries, may be employed.

When a consistency of 30 to 45 per cent is desired, a machine known as a wet machine is used. A wet machine is somewhat similar to a decker, but in it it includes a press arrangement which delivers the pulp from the machine as a sheet rather than as slush stock. To reduce screened stock to a consistency of 75 to 85 per cent requires a pulp-drying machine. Such a machine is very similar to a papermaking machine in all its essential operating details. In some cases, it actually may be a reinstalled paper machine.

Wood Pulp Bleaching. The bleaching of wood pulp (groundwood, soda, or sulfate) has for its object the production of a whiter and a better stock. In the case of groundwood, a pulp which contains nearly all the constituents of the raw wood from which it was produced, except lignin, is designed primarily to improve the natural color of the wood, discolored by atmospheric conditions or bacterial decomposition; to improve the color of pulp, discolored somewhat by a high grinding temperature; and to brighten the color of pulp containing metallic compounds, such as iron impurities. Chemical pulp bleaching, on the other hand, is an operation involving the purification of cellulose fiber by removing ligneous materials as well as other residues in the pulp.

Several different reducing agents are used for brightening the color of groundwood pulp. Dilute solutions of calcium or sodium bisulfite can be added to the pulp as it is being thickened on a wet machine, or small quantities of zinc hydrosulfites can be added continuously to the pulp stock by means of a dry feeder, or weighed amounts can be added to the stock in the batch mixer or beater.

For many years, a solution of calcium hypochlorite was the only agent commonly used for the bleaching of sulfite and soda pulps. This liquor was prepared by mixing bleaching powder with water, and then, after a short period, drawing off the clear, supernatant liquid. This practice, in recent years, has given way to the use of liquid chlorine and milk-of-lime. The first commercial installation in the United States in which a calcium hypochlorite liquor was prepared in the latter manner dates back to 1877-1919. At present, a lime bleach liquor installation includes facilities for chlorinating milk-of-lime, for settling out the insoluble material formed in the reaction, and for storing the clear liquor.

Although a considerable quantity of pulp is still bleached with calcium hypochlorite solution alone, recent advances in the technique of bleach-making have made use of it along with direct chlorination, and also sometimes with other chemical treatment of the stock. For example, in the bleaching of groundwood pulp, an operation which was considered impractical and uneconomical until only a few years ago, the procedure might include the following steps, if not more—(1) chlorination, (2) wash, (3) caustic extraction, (4) wash, (5) hypochlorite oxidation, (6) wash.

The equipment now in use for carrying out the bleaching operation has changed considerably. When the pulp is treated only with calcium hypochlorite, the equipment may consist essentially of one or more tanks, usually or horizontally positioned, each with some means for agitating the mass; or a rotary spherical pressure vessel may be used, in which case,

the rotation of the vessel serves as the means of agitating the stock. In necessity, if only a single tank is used, bleaching is carried out as a batch operation, whereas the use of a series of tanks permits either batch or continuous operation. Whatever the nature of the hypochlorite bleach solution, the bleached pulp must be washed with water to free it of trace bleach liquor as well as to remove the soluble impurities.

There are numerous possible variations in multi-stage bleaching procedure. Practice depends primarily upon the species of wood pulp, the nature of the pulping operations, the acceptance of a given system, and the use requirements of the pulp.

In the bleaching of any pulp, the four most important operating factors are time, temperature, stock consistency, and pH. These factors are intimately related, and it is the balancing of them that largely determines the economy of the bleaching operation and the quality of the resulting pulp.

After the washing operation, the bleached pulp may be further dewatered or thickened, particularly if it is to be stored or shipped, or it may be used in slush form for immediate conversion into paper.

Processing other Fibrous Materials. When it is desired to de-ink waste paper, it is common practice to use a soda ash liquor for the cooking operation. Other chemicals, used alone or in various combinations, that have been employed for this operation are caustic soda, lime, borax, soap, silicate of soda, turkey red oil, and fuel oil. Such chemically-cooked waste paper is washed carefully and then bleached much in the same manner as virgin chemical pulp.

Not all rags are boiled or cooked, but in operations where this practice is followed, particularly in mills making high-grade papers, lime, caustic soda, or a mixture of soda ash and lime are the commonly used cooking chemicals. Based on the weight of the rags, the quantity of chemicals for a rag cook may range from 1 to 10 per cent for caustic soda and from 10 to 20 per cent for lime. Cooking pressures range from 15 to 50 pounds and the cooking time, from 2 to 15 hours.

The purpose of rag cooking is to loosen dirt and to saponify or digest grease so that these materials can be removed by washing, and also to remove upon colors to facilitate later bleaching. The washing operation is carried out in a machine resembling a Hollander beater (see Condition of the Furnish) but, in addition, it is equipped with one or more washing devices. This machine is also used to reduce the cooked rags to a fibrous mass, known as half stuff, which, after bleaching with a calcium hypochlorite liquor, is ready for conversion into paper. Old rope is handled very much the same way as rags.

Cotton linters usually are purified by cooking in caustic soda solution for several hours under a pressure of 80 to 100 pounds. The quantity of caustic soda employed in such a cook approximates 15 per cent of the weight of the raw linters. The cooked fiber, after washing and bleaching, may be dried and baled for shipment or storage, or it may be used in slush form.

A milk-of-lime liquor or a liquor made by combining milk-of-lime with soda ash is usually employed for cooking straw. The amount of lime required for a milk-of-lime liquor approximates 10 per cent of the weight of

; whereas the cooking procedure calls for a steam pressure of 35 pounds for 8 or 10 hours. After the cooking operation is completed, straw, dumped from the cooker, is allowed to ripen or season in a dry room or pit for a period of several days. It then is washed and run down in much the same way as cooked rags, the essential difference in the two operations being that rags are reduced only to half-stuff while straw fiber receives its full beating treatment (see Conditioning the Sheet).

Conditioning the Furnish. Broadly speaking, the processes involved in making a sheet of paper can be divided into two phases: namely, conditioning the furnish, and sheet fabrication. The term "furnish" is used collectively to represent the fibrous and non-fibrous materials that are blended together in water suspension to ultimately produce a paper of certain desired characteristics; sheet fabrication refers simply to the production of paper on a papermaking machine.

The nature of the furnish and the method of conditioning it vary with kind and grade of paper, and even with individual mill practice. To give a few cases in point: Book paper is a general term applying to a group of papers, exclusive of newsprint, which are formulated and produced in a way as to make them suitable for use in the graphic arts. Chemical pulps, mechanical pulp, selected waste paper, and rag pulp commonly make up the fibrous constituents of such paper. Ordinarily, book paper is made of a mixture of two or three of these pulps, such as a mixture of chemical pulp and soda; sulfite, soda, and waste paper; sulfite and groundwood; etc. "Card" is also a very general term. It is used to designate certain papers which range from .006 to .012 inch or more in thickness. Chemical pulps (particularly sulfate and sulfite), semi-chemical pulp, mechanical pulp, waste paper and straw fiber serve as the fibrous raw materials for bookboards. Some boards are made from only one kind of fiber, such as straw fiber for kraft board or straw fiber (wheat, rye, or oat) for strawboard; others, from mixtures of at least two fibrous materials, such as sulfite pulp and groundwood for bottle cap board, waste paper and some chemical pulp for bookboard; and still others, from various fiber mixtures for each of several plies of the sheet, such as kraft pulp, waste kraft paper, and old newspapers for the outer plies, and chemical pulp screenings (rejects), mechanical pulp, and mixed papers for the center, in container board.

Newsprint, as previously indicated, commonly is made from a mixture of mechanical pulp and sulfite pulp, about 75 to 80 per cent of mechanical pulp and the remainder of unbleached sulfite pulp. One notable exception to this practice is the use of bleached sulfate pulp by one newsprint mill in the South for the chemical pulp portion of its newsprint paper.

The term "wrapping paper" applies to a broad classification of papers in which strength and pliability are essential characteristics. Here again is the result of a large variety of furnishes. Sulfate pulp, sulfite pulp, mechanical pulp, straw, waste papers, rope and other fibrous materials are used in its production.

Writing paper denotes paper suitable for use with typewriter, pen and pencil, or for printing. The fiber furnish commonly determines

sheet quality. It ranges from 100 per cent rag, mixtures of rag and chemical pulp, 100 per cent chemical pulp, to mixtures of chemical and mechanical pulps.

The kind of paper being made determines the need for non-filling raw materials in the furnish as well as the material or materials to use. A few of the more common materials used for this purpose are rosin size, dyestuffs, sodium silicate, starch, clay, titanium pigments, talc, blank, precipitated calcium carbonate, and zinc sulfide. Each of these materials as well as numerous others, are used to impart very definite character to finished papers.

The equipment used for blending the various components of the furnish as well as for hydrating and altering the surface character of the fiber, has witnessed numerous changes in design within recent years. In brief, stock conditioning equipment may be classified generally into the following types—Hollander beater, jordan, disc, hydraulic, and rod mill.

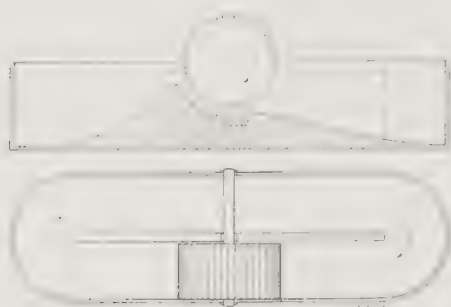


FIGURE 131.—The Hollander beater; upper drawing, a vertical cross-section through the roll side; lower drawing, a top view.

The Hollander beater has been used in papermaking for many years and is characterized by an oval-shaped tub with an impartial partition extending lengthwise through its center, a hooded, horizontally positioned roll laterally placed bars on its face, and a bed-plate arrangement so located in the bottom of the tub to permit bar-to-bar action between it and roll. In fact, so important has been the functioning of the machine, the aphorism, "Paper is made in the beater," has long been associated with the industry.

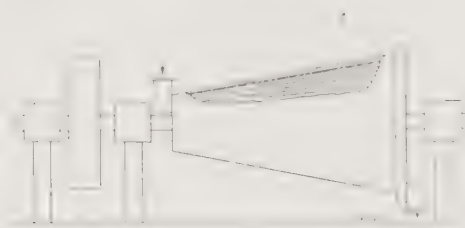


FIGURE 132.—The jordan or conical refiner.

The jordan consists essentially of a horizontally positioned conical shell within which rotates a correlative cone-shaped plug. Both the inside of the shell and the outer surface of the plug are fitted with bars; and, through adjustment of the plug, the desired bar clearance between the shell and plug is established.

Designs of disc-type machines in use include both single disc and double disc units with the respective disc or discs rotating in a vertical plane.

In the hydraulic system, stock is impinged from a jet at high velocity against a target of special design or against an oppositely directed jet of water. In the rod mill, stock is acted upon by the crushing action of a comparatively heavy weight of metal rods which roll over one another in a revolving, horizontally positioned, cylindrical shell.

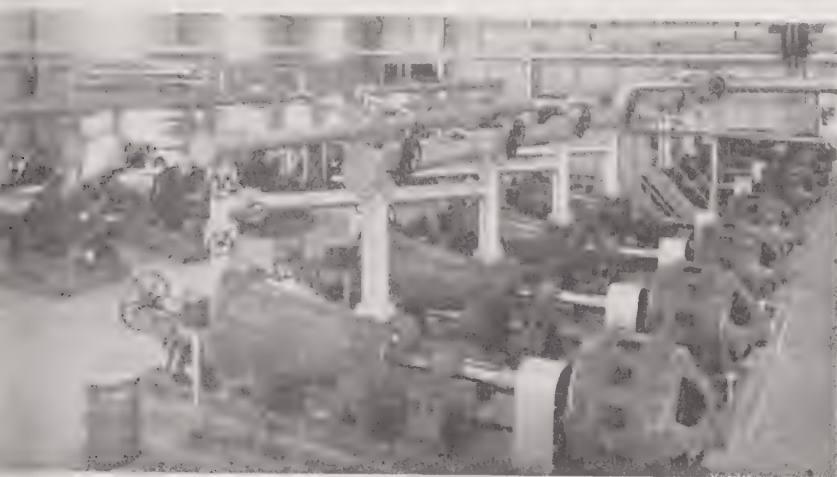


FIGURE 133.—A double row of jordans in a large paper mill. (Courtesy of *Paper Industry and Paper World*.)

There are also a number of other designs of stock-conditioning equipment, but in each case, like that of the equipment already mentioned, it has for its purpose the conditioning of the furnish to an end-point which will give the desired results when fabricated into paper. To supplement the work of the conditioning equipment and to permit final control of the stock before fabrication is a jordan installation. If jordans are being used for the initial or primary stock treatment, as is the case in a number of mills, particularly in the South, they may be grouped with the finishing jordans in a single convenient arrangement.

After the stock has passed through the finishing jordans, usually at a consistency of about three per cent, it is diluted to a consistency of approximately one per cent. At this consistency it is ready for screening and possibly other purification, after which it is delivered to the paper machine. The purpose of this screening operation is two-fold—first, to remove as much of the undesirable solids from the stock as possible; secondly, to obtain a better separation of fibers so that, when the stock is delivered to the paper machine, better felting of the fibers will result. In most mills, this screening of the stock completes the conditioning of the furnish; but further purification is accomplished by some mills in a supplementary operation if a more dirt-free sheet is desired.

The screening of the stock is accomplished in machines designated as paper machine screens as contrasted with the pulp screens of the pulp mill. Paper machine screens commonly are of two types—either diaphragm or flat (similar to the flat screen of the same designation used for screening pulp), or rotary.

There are two types of rotary screen—the inward flow and the outward flow. In the inward flow screen, accepted stock passes inwardly from a vat through slots of a screen-plate cylinder positioned within it. The cyl.

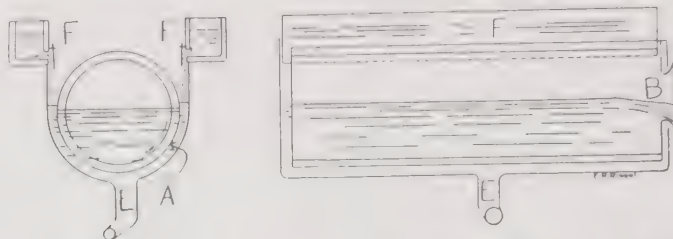


FIGURE 134.—Inward flow screen for paper stock. *A*, slotted screen which rotates; *B*, open discharge for cleaned stock; the vat itself is shaking in horizontal plane; *E*, waste pipe for tailing removal; *F*, flow boxes. Driving and shaking mechanism not shown.

is open at one end, and this end serves as the discharge for the accepted stock. Rejects, in turn, are removed from the bottom of the vat. Conversely, in the outward flow screen, stock to be screened enters the screen plate cylinder. The accepted stock passes through the openings in its plate into a vat beneath it; the rejects, in turn, are removed from within the cylinder by the use of a discharge pan located within it.

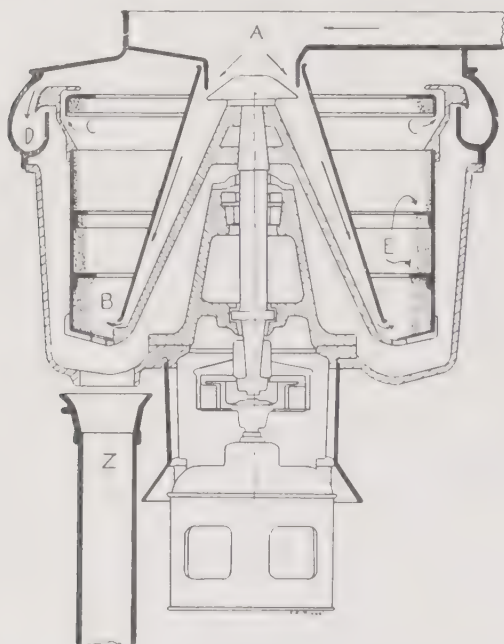


FIGURE 135.—Centrifugal device for removing dirt from paper stock. *A*, raw stock inlet; *B*, mat with dirt retained by angular baffles *E*; light dirt caught by annular skimmer *C*; *D*, cleaned stock, with outlet to paper-making machine; *Z*, waste pipe for washings.

Dirt too small in size to be rejected in screening may be separated from the screened stock, if necessary, by equipment which, for its function depends upon the difference in specific gravity of the dirt and the fiber. Such equipment may employ centrifugal force to effect the separation. Separation may be accomplished by increasing considerably the weight

ential between the dirt and the stock by use of a pressure differential.

abrication of the Sheet. The making of a sheet of paper on a paper machine involves dewatering of the stock and the surface finishing of the sheet. The dewatering of the stock must be accomplished in a manner that produces a sheet of uniform structure and thickness. It is done through application, in combination, of natural drainage, induced drainage by vacuum, roll pressure, and heat; while surface finishing of the sheet, in general, is accomplished by rolling friction. These operations are performed by either one of two types of paper machine—a fourdrinier machine or a cylinder machine.

The fourdrinier machine is characterized by the use of a traveling wire, commonly designated as the wire, for the felting of the sheet. This wire is supported by tube rolls in such a way that the portion of it receiving the wet stock from a head box immediately preceding is traveling forward in a horizontal or nearly horizontal plane. In addition to traveling forward, the wire usually is given a sidewise motion or shake. This move-

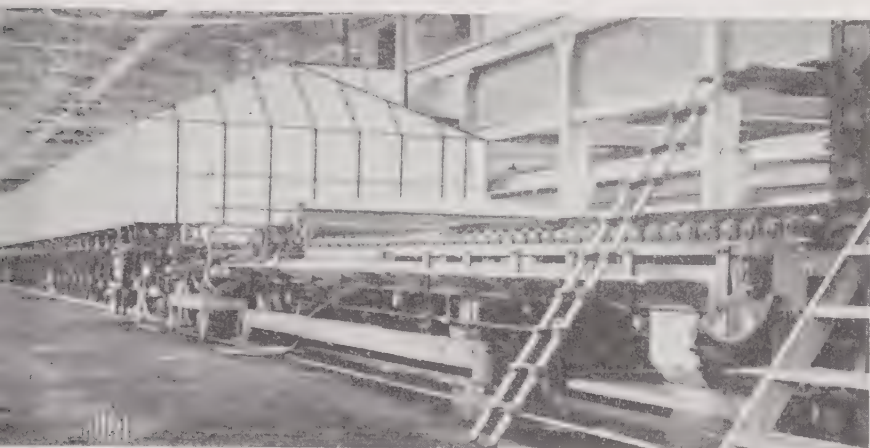


FIGURE 136.—Fourdrinier paper machine with sheet-forming section in immediate foreground. (Courtesy of Beloit Iron Works.)

effects better intertwining of the fibers upon the surface of the wire as water in which they are suspended drains through it. Removal of water from the forming sheet is hastened by the addition of suction boxes to the side of the sheet-carrying portion of the wire. Considerable water removed by natural drainage is evacuated through these boxes by applying partial vacuum to their drainage area.

By the time the sheet reaches the forward end of the wire, sufficient water has been removed from it so that it can support its own weight. At this point it is conveyed by means of woolen felts or blankets through a series of nip-type presses. Not only do the presses remove additional water from the wet sheet but they also compact it. The compacted sheet then passes through the dryer section of the machine where approximately two pounds of water are removed from it for each pound of paper produced. This section

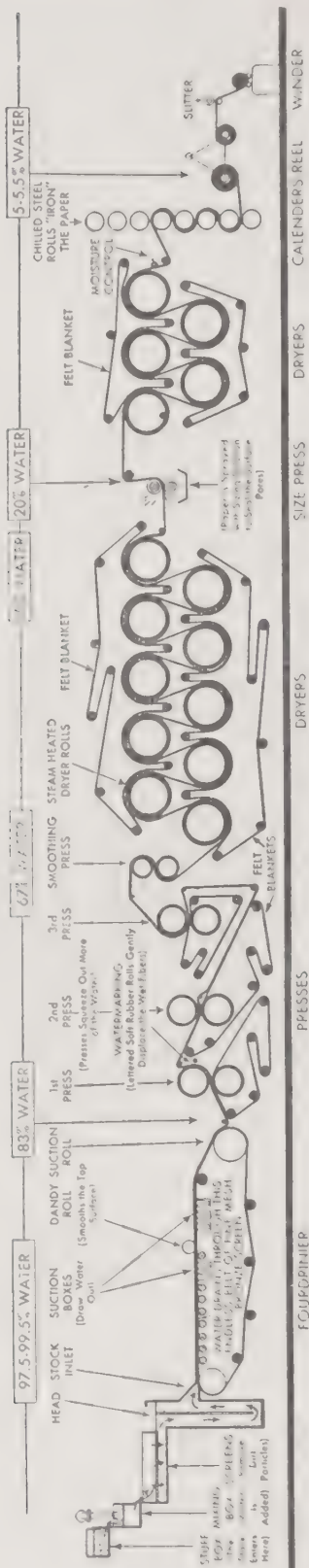
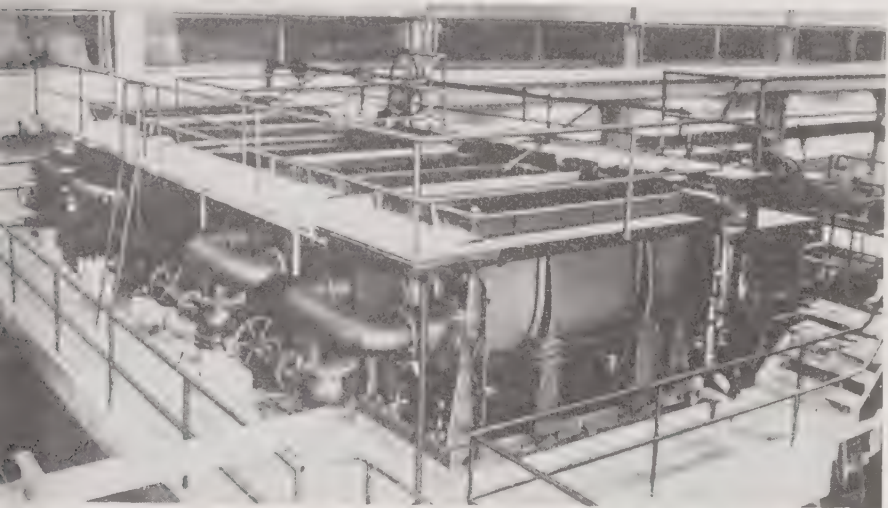


Figure 137.—Diagram of a modern foundrier machine showing how paper is made upon it. (Courtesy of the Hammervill Paper Company, Erie, Pa.)

only is made up of a series of steam-heated cast-iron cylinders, the number and size of which depend upon the grade of paper being produced upon the speed at which the machine is operated.

After the drying of the sheet, it is necessary to improve its surface. This finishing operation is accomplished by passing the sheet through a calender stack of horizontally positioned, highly polished, chilled cast-iron rolls known as the calender or calender stack. In this arrangement, power is applied to the bottom roll, the other rolls revolving simply through friction contact.

After the sheet leaves the calender it is wound into a large roll by means of a reel. The reel is designed to permit continuous operation of the machine. When a roll reaches a suitable diameter, the sheet is broken and another roll started. The first roll is then slit and rewound into rolls of the proper width for marketing or for immediate conversion into a variety of paper products.



138.—Installation comprising four inward flow screens serving stock fed to a fourdrinier newsprint paper machine. (Courtesy of the Bird Machine Company, Easton, Massachusetts.)

The sizes of fourdrinier machines, commonly designated by width of sheet, vary widely. The widest fourdrinier in North America has a wire width of 304 inches. As originally installed, this machine had a length of 100 feet. It weighed approximately 2100 tons, the rolls in the calender alone, an eight-roll stack, weighing 150 tons. Likewise, the dryer included 48 drying cylinders, each with a diameter of 60 inches and a length of 302 inches. These dryers weighed 13 tons apiece. Operating on newsprint, the daily productive capacity of this machine considerably exceeds 200 tons.

The cylinder paper machine, differing from the fourdrinier machine principally in the manner of felting the sheet, receives the paper stock in one or more vats. Partially submerged in each vat is a cylinder mold with a

surface of wire cloth. As the mold revolves, the sheet is felted to the cloth by the drainage of water to the interior and from which it is charged. The wet sheet thus formed is removed from the unsubmerged portion of the cylinder by means of an endless woolen felt or blanket, which also carries it through a series of squeeze rolls and a roll-type press similar to that of a fourdrinier machine. The squeeze rolls and the press compact the sheet and remove considerable water from it. More water is removed and the sheet is further compacted by passing the sheet through two or possibly three additional presses. After the pressing operation, the sheet passes over steam-heated drying cylinders, through a calender arrangement, and to a reel just as in the case of the fourdrinier machine.

When more than one vat is used in combination, five or six cylinder machines being rather common and even more cylinders being used in some instances, a sheet of several plies, one ply for each mold, is built up of

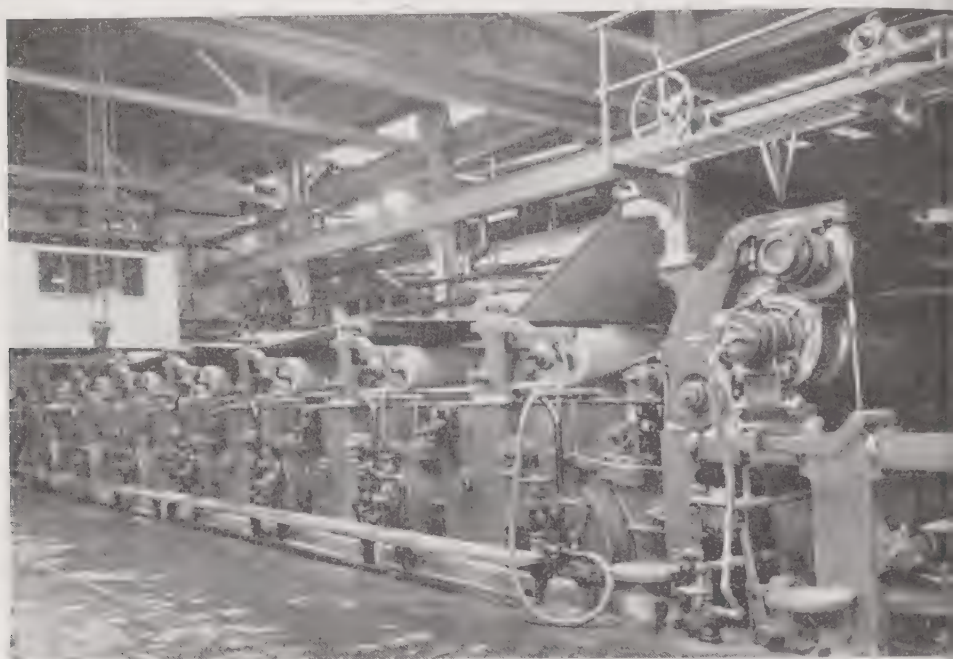


FIGURE 139. Wet end or forming section of multi-cylinder papermaking machine. (Courtesy of Black-Clawson Co.)

single felt which contacts the unsubmerged area of each cylinder. The multi-layer sheet, like the sheet from a single cylinder machine, is subjected to mechanical pressure both to compact the fiber mass and to remove water from it. Then, too, the pressing operation brings the several layers closely together so that, after drying, they form to all intents and purposes an integrated sheet.

There are several modifications of the fourdrinier and cylinder type paper machines. Probably the two most important of these modifications would be the Harper fourdrinier and the Yankee machine. In the Harper fourdrinier machine, the wire runs away from the presses rather than to them, the first or wet end section of the machine being in reverse to

fourdrinier. The sheet formed on the wire is removed from it by a felt which, extending over the forming section, delivers it to the press end of the machine. This feature of the machine makes it especially factory in the manufacturing of lightweight papers.

The Yankee machine is characterized by its dryer arrangement. It features a single, highly-polished, large diameter dryer, with or without auxiliary dryers. The range in diameter for a Yankee dryer usually is from 9 to 15 feet. Such a dryer imparts a glossy finish to one side of the sheet, and is particularly adapted to the manufacture of thin and medium weight papers such as are used in the lining of duplex paper bags, toilet paper, etc.

TABLE 47.—*U. S. paper and paperboard production by kinds (1940).*

	Quantity (Short Tons)		Quantity (Short Tons)
Newsprint	1,056,304	Absorbent paper	129,410
Groundwood printing and specialty papers..	550,453	Building paper	682,460
Book paper	1,693,432	Other paper	60,120
Writing paper (fine)....	599,452	Boards	6,449,548
Wrapping paper	2,500,818	Aggregate	14,483,709
Issue paper	761,712		

Industrial chemistry has played an important part in the development of the modern pulp and paper industry. The very nature of its processing operations, which have been only briefly outlined, has demanded it. Likewise, in all probability, its role will become of constantly increasing importance.

TABLE 48.—*U. S. paper and paperboard production by States (1940).*

State	Quantity in Short Tons	State	Quantity in Short Tons
New York	1,455,573	Oregon	310,870
Michigan	1,239,381	Minnesota	300,563
Maine	1,073,039	Indiana	252,435
Wisconsin	1,072,150	Connecticut	174,496
Ohio	997,867	New Hampshire	169,059
Pennsylvania	987,650	Maryland	161,709
New Jersey	780,151	North Carolina	154,232
Louisiana	753,752	Vermont	77,046
Illinois	610,769	Texas	71,037
Washington	600,180	West Virginia	51,825
Virginia	577,625	Delaware	29,777
Massachusetts	518,764	Other Southern States ¹ ..	1,035,068
Florida	392,003	Other States ²	307,606
California	329,082	U. S. total	14,483,709

Alabama, Arkansas, Georgia, Mississippi, South Carolina.
District of Columbia, Iowa, Kansas, Missouri, Rhode Island, Tennessee.

OTHER PATENTS

U. S. Patent 1,837,309, production of sulfite pulp and recovery of the acid employed;
2,066,000, process of making pulp, subjecting the treated material to a steam pressure of 250 pounds sq. in. and discharging at that pressure so that the material is broken and thoroughly disintegrated; 2,031,974, recovery of chemicals from waste liquor; 2,069,185, manufacture of vanillin from waste sulfite pulp liquor.

PROBLEMS

A soda pulp digester has a capacity of 820 cubic feet. It contains at the end of the run 220 cubic feet of cellulose fibers. In the remaining space, a volume equivalent to 100 cubic feet of cold 5 per cent caustic soda, with specific gravity of 1.05, is intro-

duced. What was the weight of the cold caustic liquor, how much caustic in pounds did it contain, and what was the volume of the 5 per cent caustic soda in gallons?

2. A sulfite pulp digester has a capacity of 3000 cubic feet; it contains a 6 per cent calcium bisulfite solution to the extent of two-thirds of its volume, measured. Let the specific gravity of the solution be 1.07. How much calcium bisulfite is present, how much sulfur dioxide, and how many pounds of sulfur would be required for the production of one-half this quantity of sulfur dioxide?

3. A wood contains 50 per cent cellulose. It is desired to produce 56 tons of certain paper per day, from chemical pulp. How many cords of wood will be required using the values given in the text? The yield of paper on the basis of cellulose in wood is 90 per cent.

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The chief natural fibers used for articles of clothing are cotton, linen, and silk; to these have been added through the chemist's ingenuity a number of synthetic fibers, among which are rayon, acetate rayon, Vinylon, and Nylon.

Chapter 22

Synthetic Textile Fibers*

Today the most important synthetic textile fiber is rayon. Chemically developed as early as 1664 but not produced commercially in France until 1891, rayon has risen rapidly to a position of prominence in the textile industry. This prominence is indicated by the fact that in 1940 rayon was produced in greater quantities throughout the world than was wool.

Rayon may be defined as a man-made textile yarn or fiber whose chemical base is cellulose. More exactly defined, "Rayon is the generic term for filaments made from various solutions of modified cellulose by pressing or extruding the cellulose solution through an orifice and solidifying it in the form of a filament." This definition covers those fibers composed of a chemical compound of cellulose (e.g., cellulose acetate) as well as those produced by the regeneration of cellulose from a chemical solution (e.g., viscose, cuprammonium, or nitrocellulose).

The term "rayon" was coined in the United States in 1924 for the purpose of replacing the term "artificial silk" as a name for these cellulose-based synthetic fibers. This term is now generally accepted throughout the world as the generic name for this family of textiles.

Two primary products now are made by the industry, namely, continuous filament rayon yarn and rayon staple fiber. By way of differentiation, continuous filament yarn may be described as being made of a number of fine, continuous rayon filaments, grouped and lightly twisted together. On the other hand, rayon staple fiber is made by cutting rayon filaments into short lengths which are subsequently spun into yarn in the same manner as cotton or wool. The resulting textile yarn is called "spun rayon yarn." Other primary products made by the rayon industry are rayon bands and ribbons (artificial straw) and rayon monofil (artificial horsehair).

GROWTH OF RAYON PRODUCTION

The growth of the rayon industry throughout the world in the fifty years of its existence has been unusually rapid. In 1890 the world output of rayon amounted to a mere 30,000 pounds, whereas in 1940 it was 2,380,000 pounds. The more important rayon-producing countries and their relative outputs in 1940 are shown in Table 48a.

Although the United States in 1940 was the third largest producer in the world of rayon output, it was by far the world's greatest single producer of continuous filament yarn accounting for 34 per cent of the world's output of rayon product.

The uses of rayon are varied and numerous. Its application in apparel-making is particularly important. For further information on rayon, in collaboration with Mr. Stanley B. Hunt, Textile Economics Bureau, Inc., 19 East 40th Street, New York, N. Y.

TABLE 48a.—World rayon production (1940).
(Rayon filament yarn plus rayon staple fiber.)

	Millions of Pounds	%
Germany	825	35
Japan	525	22
United States	471	20
Italy	325	14
Great Britain	150	6
All others	84	3
Total	2380	100

type fabrics is now well known to all. Great quantities of rayon are in the manufacture of dresses, underwear, hosiery, linings, elastic goods, in numerous other items of men's, women's, and children's apparel. Household uses of rayon include rugs, carpets, blankets, upholsteries, drapes, tapestries, quilts, bedspreads, table linens, etc. There is also a growing use for rayon in industrial products. Noteworthy here is its use in automobile and airplane tires.

Besides its application in these many civilian products, rayon is playing a very important part in this country's war effort. Substantial amounts of rayon are being used in tires for the Army's mechanized equipment, in airplane tires, in self-sealing gas tanks for bomber and fighter craft, in flare parachute cloth, in cartridge and powder bag cloth, in laying and fragmentation bomb parachute cloth, in paratroop jumpsuits, wire insulation, helmet linings and assemblies, uniform linings, and in many other uses.

The reasons for the increase in the use of rayon may be attributed to three factors: style, serviceability, and price. Because rayon is a product of chemistry, its production is accomplished only under rigid, chemical standards of control. Thus its quality and uniformity are assured. At the same time, however, its chemical nature makes it possible for rayon producers to develop many innovations in fiber structure and character, which in turn are given to the consumer in new fabrics. Rayon's affinity for dyes permits almost endless color combinations in fabrics, thus appealing to the fashion habits of the consumer.

The style and serviceability features of rayons are available to the consumer at price levels that are within the reach of all income groups. The prices of rayon filament yarn and staple fiber have been steadily low during the years. This tendency has been the result of the progressive improvement in the technique of rayon manufacture, which at the same time has improved the quality of the product. For example, the price of rayon denier yarn in 1920 was \$6 per pound. The 1941 price for this same denier yarn, of greatly improved quality, was only 53¢ per pound.

METHODS OF RAYON MANUFACTURE IN THE UNITED STATES

Rayon filament yarn is produced by three methods in the United States, namely, the viscose process, the cellulose acetate process, and the cuprammonium process. From 1920 to 1934 rayon yarn was also produced by the nitrocellulose process. This process is the original method of rayon manufacture, invented in 1884, and patented by Count Hilaire de Chabaz.



FIGURE 140.—The rayon plant at Spruance, Virginia, of E. I. du Pont and Company, as seen from the air (by permission).

donnet. Yarn by this method was first commercially produced at Besançon, France, in 1890. Although this process has been discontinued in the United States, it is still used in Brazil and Hungary; however, the output of this type yarn is very small.

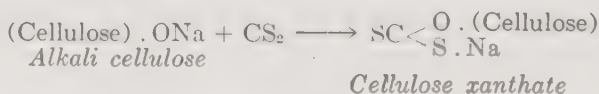
The fundamental principle of rayon yarn manufacturing is the same, regardless of the process of manufacture used. A cellulose solution of proper viscosity is prepared and subsequently forced through tiny openings into a medium which coagulates these fine streams as they emerge. By this coagulating action, filaments of cellulose or a cellulose compound are formed which are then conditioned, processed, twisted, packaged as required, and then shipped to textile fabricators.

The size of the filaments so produced are measured in terms of denier. The denier of a yarn may be defined as the weight in grams of 9000 meters of the yarn. Thus a yarn is said to be 150 denier, if 9000 meters of it weigh 150 grams. Therefore, the lower the denier the finer the yarn; conversely, the higher the denier the coarser the yarn.

The Viscose Process.

The viscose process is at the present time the most widely used. United States production of viscose yarn in 1941 accounted for about 60 per cent of the nation's total yarn output; the proportion of world production is somewhat higher. The principal raw materials used by this process are dissolved wood pulp, refined cotton linters, carbon disulfide, sulfuric acid, caustic soda, glucose, ammonia, magnesium sulfate, sodium carbonate, sodium aluminum sulfate, sodium sulfide, zinc sulfate, and other chemicals in small quantities.

This process is based on the discovery made in 1892 by two English chemists, Gross and Bevan, that mercerized, or alkali, cellulose forms a definite, though unstable, compound with carbon disulfide. This compound, called cellulose xanthate, is a yellow solid and its formula may be written



Cellulose xanthate is soluble in dilute caustic soda and from this solution the regenerated cellulose is precipitated by the action of an acid. Simply stated, the chemical reactions of this process are as follows: Alkali cellulose is combined with carbon disulfide, and the resultant is dissolved in dilute caustic soda, producing a viscous solution called viscose. This solution is then sent to the spinning device and the emerging fine streams of the solution are coagulated by a bath containing sulfuric acid and other chemicals. A more detailed description of the process follows:

Sources of Cellulose. The sources of cellulose for this process are either wood pulp or refined cotton linters pulp. The American viscose rayon industry at present depends more on wood pulp than on cotton linters pulp for its cellulose supply. The alpha-cellulose content of wood pulp for this process ranges from 88 to 92 per cent. Especially refined cotton linter pulp approximates 98 per cent alpha-cellulose content. Wood pulp and

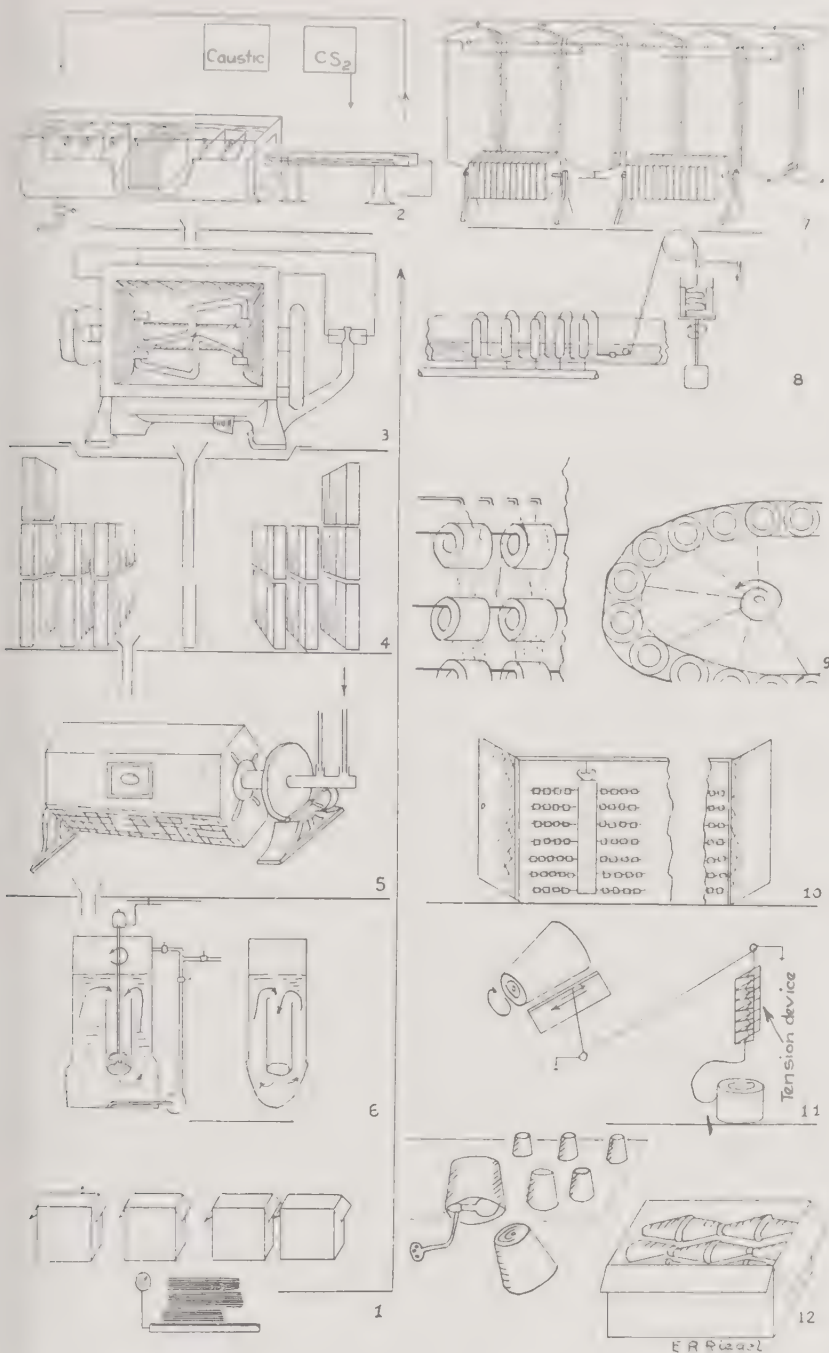


FIGURE 141.—Flow sheet for the viscose rayon process.

1. sulfite sheets storage.
2. caustic swelling tank
3. shredder
4. aging of alkali cellulose crumbs
5. xanthating churn
6. mixer for dissolving the xanthate in caustic

7. viscose aging tank
8. spinning machine
9. left, desulfurizing, bleaching, washing of cake; right, centrifuging
10. drying
11. winding into cones through tension device
12. inspection and shipment

cotton linters pulp arrive at the rayon-producing plant in bales of sheets. These sheets of pulp are stored in pulp storage rooms and for several weeks in an atmosphere of controlled temperature and humidity.

Alkali Cellulose. When ready to be put into process, the pulp is fully selected for steeping, which is merely a mercerization process. The pulp is placed in a steeping press which is then filled with a NaOH solution of 17 to 18 per cent concentration at a definite temperature. The



FIGURE 142.—The alkali cellulose shredder in a rayon plant. (Courtesy of E. I. du Pont de Nemours and Company, Inc., Rayon Department.)

is allowed to soak for about two hours. In this stage of the process α -cellulose remains insoluble, but the β - and γ -cellulose are leached by solution with the caustic soda. The sheets of cellulose are then pressed together by a hydraulic ram to squeeze out the caustic soda, which then is drained out of the tank. The resulting product is called alkali cellulose. The liquid drained out of the storage tank is sent to dialysis for purification and reuse.

The soft alkali cellulose sheets are then dropped into shredder machine where the alkali cellulose is reduced to soft crumbs by a shredding operation.

loosens, blends, and fluffs up the cellulose fibers. During this entire operation the alkali cellulose is kept under a temperature of about 18 to 20°. The crumbs are then removed from the shredder and put into steel

containers. These containers are sent to a temperature-controlled aging room where the cellulose undergoes a change in its molecular structure during the several days of aging.

Xanthate. After aging, the alkali cellulose is ready for xanthation. In this operation the alkali cellulose is converted into another chemical compound, cellulose xanthate, by treating it with carbon disulfide for several hours under controlled temperatures. This operation is performed in a



FIGURE 143. —The tanks in which the viscose is stored, aged, filtered, and liberated from bubbles by applying a vacuum. (Courtesy of E. I. du Pont de Nemours and Company, Inc., Rayon Department.)

churn which rotates horizontally as the carbon disulfide is introduced is absorbed by the cellulose the color of the cellulose changes from white through gradations of yellow to orange. When the latter color stage has been reached, the xanthating process is completed. The excess carbon disulfide vapors are drawn off and the xanthate discharged into a viscose or dissolving machine.

Spinning Solution Preparation. This dissolving machine is filled with dilute caustic soda before receiving the charge of xanthate. The xanthate is dissolved in the NaOH solution and the resulting solution contains al-

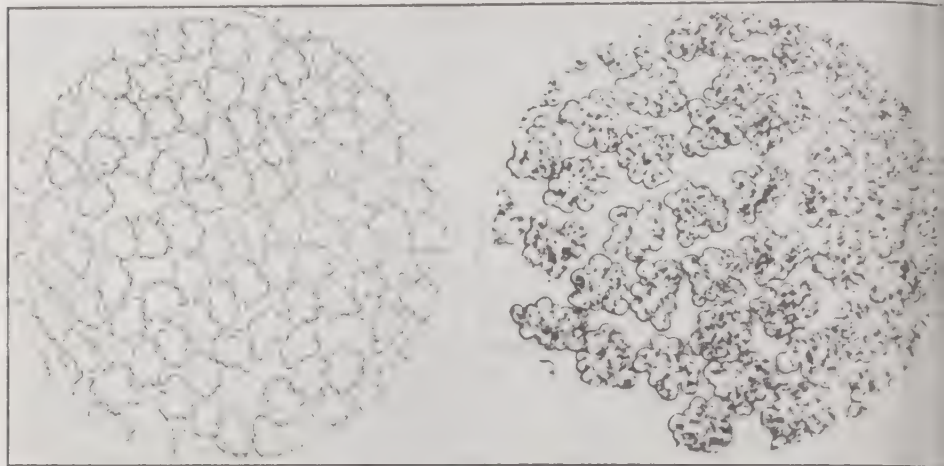


FIGURE 144.—Photomicrographs of a cross-sectional slice of the rayon thread, showing the several filaments, for a clear viscose (left), and for a delustered one (right). Courtesy of the Research Laboratory, Technical Division, Rayon Department, E. I. du Pont de Nemours and Company, Buffalo.

7.25 per cent cellulose and 6.5 per cent sodium hydroxide. It is brown green in color and viscous in character; hence the name "viscose."

If no delustering agents are added, this solution will be used for spinning bright viscose yarn. For dull and semi-dull yarns there is added at this stage a dispersion of titanium dioxide whose average particle size by surface mean is 0.56 micron. This delusterant becomes an integral part of

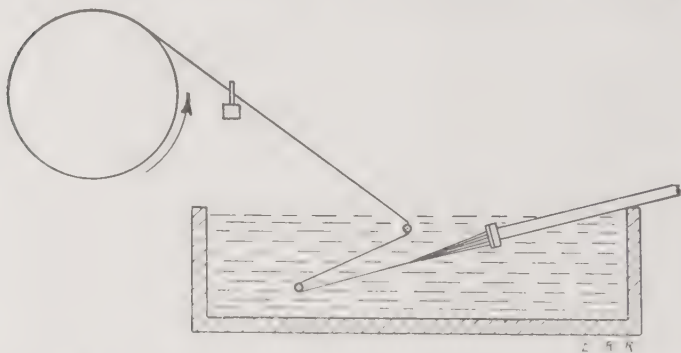


FIGURE 145.—A spinner for viscose silk.

yarn and, therefore, is permanent; it can never be rubbed out or washed out. Delustering is possible because titanium dioxide has a greater refractive index than that of the regenerated cellulose.

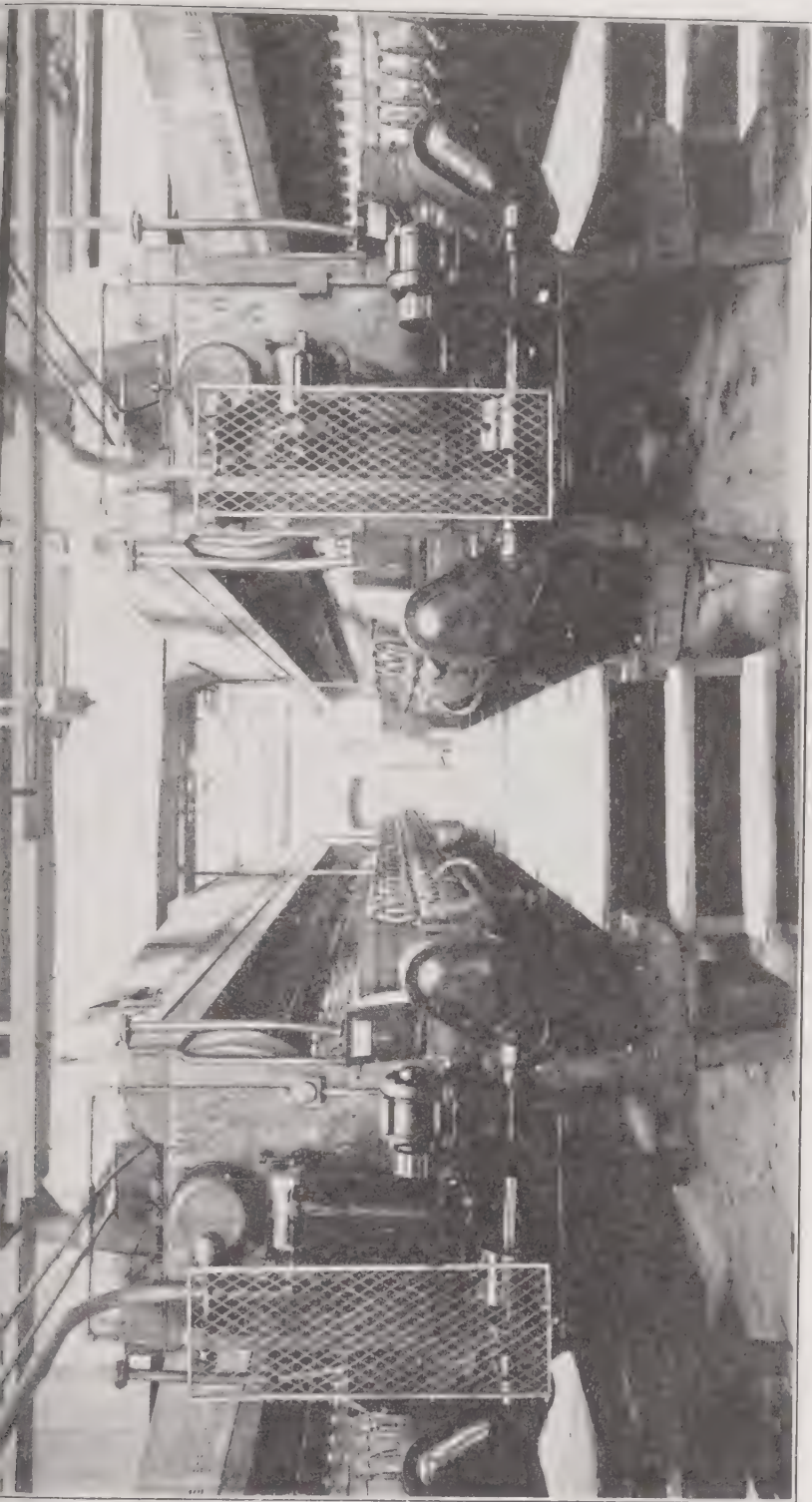


FIGURE 146.—A view of the spinning machines in a rayon factory, bobbin type—the spinnerets proper are inside the acid trough, at the end of the bent tube which surmounts the candle filters. The latter are well shown in a partly withdrawn position, especially at the extreme right of the picture. Many other details are visible. (Courtesy of the Viscose Company, New York.)

The viscose solution is then filtered to remove any foreign matter undissolved cellulose, and is finally placed in a storage or ripening tank. In this tank any air bubbles are removed and the solution is matured several days under strict temperature control. While the solution is aging or ripening, the temperature is maintained at 16° C. (61° F.). The longer the viscose ripens, the higher the temperature, the more readily does it floc, and the lower the salt index. The viscosity-time curve has a sharp break, and the aim is to spin the viscose close to the break, but before it is reached.

To test the ripening of the viscose, one drop is placed in a salt solution and its coagulation observed. The salt solution is made up by running 4.2, 6 cc., or more, of a strong stock solution into enough water to make whole 40 cc., in an Erlenmeyer flask, which is then shaken one-half minute. The proper action is the division of the drop into 3 flocks. The less viscous solution requires more salt for coagulation. The ripening is right when the "salt index" is 3.2 to 4.2. A variation in ripeness means variations in a number of physical properties, such as tensile strength, spinning properties, and dye acceptance. For a short time, the properly aged solution may be preserved unchanged in the right state for spinning at 0° C. (32° F.).

Spinning and Coagulation of Viscose Solution. In this operation the conversion of the cellulose solution to a textile fiber is accomplished. The viscose solution is pumped to the spinning machine and delivered to the spinneret, which may be described as a small nozzle containing many minute orifices.

This spinneret, or jet, is already immersed in a spinning or coagulation bath into which the fine streams of viscose solution are extruded. A typical spinning bath is composed of warm water at 40° to 45° C. (104° to 113° F.) containing 8 to 10 per cent sulfuric acid, 13½ to 20 per cent sodium sulfate, approximately 1 per cent zinc sulfate, and from 4 to 10 per cent glucose. When the viscose solution, comprised of about 7 per cent cellulose and 3 per cent caustic soda, enters this bath the fine streams of viscose coagulate.

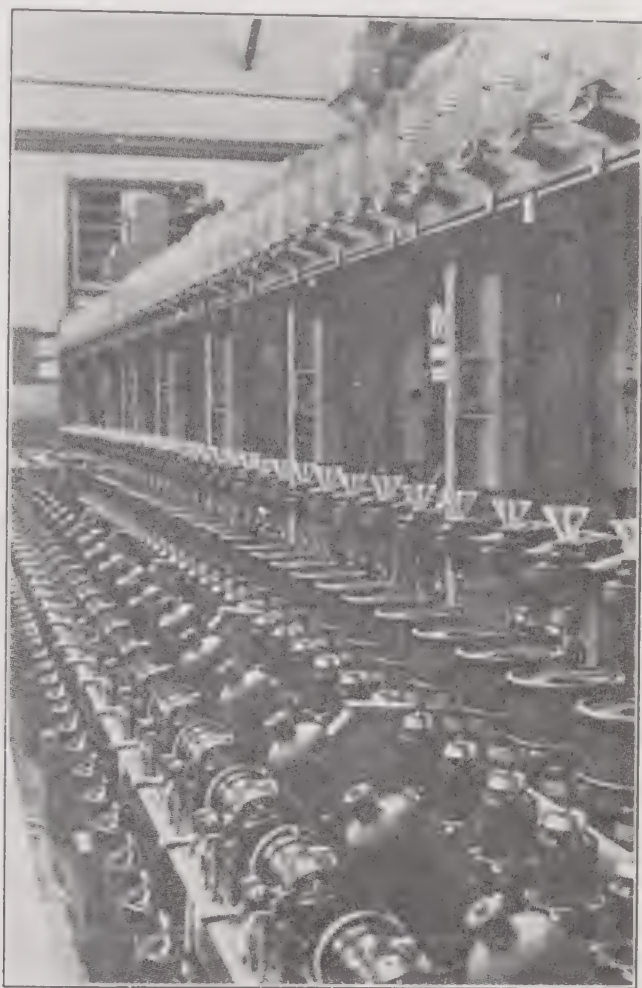
The action of the acid in the bath on the alkali of the viscose solution produces sodium sulfate, which remains in the bath: $2\text{NaOH} + \text{H}_2\text{SO}_4 = \text{Na}_2\text{SO}_4 + 2\text{H}_2\text{O}$. At the same time, part of the sulfur passes out as hydrogen sulfide which is removed by air suction; its formation is shown by the reactions: $3\text{CS}_2 + 6\text{NaOH} = \text{Na}_2\text{CS}_3 + \text{Na}_2\text{CO}_3 + 3\text{H}_2\text{O}$, and $\text{Na}_2\text{CS}_3 + 3\text{H}_2\text{O} = \text{Na}_2\text{CO}_3 + 3\text{H}_2\text{S}$. Another part of the sulfur remains as elemental sulfur on the fiber. By circulating to a correcting tank, the composition of the bath may be kept constant. The yarn passes through the spinning bath at the rate of 70 to 100 meters per minute.

Systems of Spinning. Three systems of spinning viscose yarn are in use today in this country—the pot, bobbin, and continuous processes. In the pot system the yarn passes horizontally through the spinning bath and over a rotating wheel called a "Godet Wheel" and down into a centrifugal pot where the entering yarn is coiled by centrifugal force on the wall of the pot. This pot, about 7 inches in diameter, is rotated at from 6000 to 10000 rpm. The revolution of this pot causes individual filaments to be lightly twisted into a yarn—2½ turns per inch—and in addition throws off, through perforations in the wall of the pot, much of the spinning bath solution.

saturates the yarn. When a pot is filled, which usually takes several minutes, the cake of yarn is doffed and removed from the spinning machine. The yarn then goes through several finishing processes before reaching its final state. These operations are discussed in detail later.

In the bobbin system of spinning, the yarn is wound on a perforated drum which is located directly over the coagulating bath. In this system the viscose solution is ejected vertically upward and out of the spinning

FIGURE 147.—A bank of the bucket spinning machine for rayon, with the bucket removed to show the working parts. Beginning at the left below, the parts are: switch for motor, lamp, candle filter (seen at an angle), motor driving the bucket, bucket with cover and cover lock, and near the end, feed wheel. (Photo. Dr. Paul H. Hoff.)



machine, as compared with the horizontal extrusion of the pot system. However, in the bobbin spinning system no twist is imparted to the filament; twisting is done in a later operation. The yarn, after spinning, undergoes subsequent purification treatments similar to those given to yarn by the pot system.

The newest of the spinning systems is the "continuous" process, whereby the yarn passes from the spinning bath, which is located at the top of the spinning machine, down over a series of rotating spools. Each thread passes over 9 spools which are located one below another and each of which

represents a stage in the processing treatment of the yarn. At the end of this machine, the yarn is dried and run onto the final bobbin as finished yarn. The complete operation from the spinning bath through all the drying, chemical treatments, drying, and twisting takes only about $4\frac{1}{2}$ min. by this process.

Finishing of Pot and Bobbin Yarn. Unlike the continuous process, yarn spun by the pot and bobbin systems must be treated and finish special operations after leaving the spinning machine. These after-treatments consist of washing, desulfurizing, bleaching, drying, and packing.

After the cake or bobbin yarn has been removed from the spinning machine, it is washed on the bobbin, in the cake form or, also in the cake, the yarn may be reeled into skeins before washing. This washing is with warm water, and removes the remaining spinning bath from the yarn. After drying, the yarn is desulfurized by passing it through alkaline sodium sulfide, after which it is washed again. It may then be bleached with sodium hypochlorite and again washed thoroughly. These treatments, although typical, are often varied. The yarn is finally dried, wound on cones, cops, tubes, or skeined and then inspected, graded, soiled, and shipped.

Raw Material Consumption. The approximate poundage consumption of raw materials per pound of viscose-process rayon yarn is as follows: wood pulp and cotton linters, 1.15 to 1.25; caustic soda, 1.4; carbon disulfide, 1.0; sulfuric acid, 1.7 to 1.9; glucose, 0.5; and all other chemicals, 0.4. In addition, from 100 to 200 gallons of pure water are required to produce one pound of viscose rayon yarn. These figures represent gross consumption of raw materials and chemicals and do not take into account any recovery thereof.

Cellulose Acetate Process

The acetate process of rayon yarn manufacture ranks second only to the viscose process in volume of production. United States production of acetate yarn in 1941 amounted to 36 per cent of the total annual output. The principal raw materials used by this process are refined cotton linters, softwood high alpha dissolving wood pulp, acetic anhydride, glacial acetic acid, sulfuric acid, acetone, titanium dioxide, and water.

This process is based on the original work of Naudin and Schutzenberger in 1865, although the full development of this process on a commercial scale did not come about until after the World War under the direction of Henri and Camille Dreyfus. Since the early twenties its growth has been extremely rapid, both here and abroad.

The following are the general principles and stages of operation in the manufacture of acetate yarn.

Acetylation. The first operational step in this process is the acetylation of the cellulose. Batches of cotton linters or wood pulp which have been pretreated with acetic acid, or some other activating chemical, are placed in an acetylator. Before putting these linters into the acetylator, however, the machine is charged with a solution containing a mixture of acetic anhydride and glacial acetic acid, together with a small quantity of concentrated sulfuric acid as a catalyst.

the pretreated cellulose is gradually added to this charge with continuous mixing. During the period of acetylation the temperature of the solution is rigidly controlled and the reaction is carried to completion, that is, degree of acetylation approximating the tri-acetate which dissolves in acetylating mixture. In the final stage of acetylation the solution is a very viscous, semi-transparent, acrid-smelling fluid and is commonly called **primary acetate**.

Hydrolysis of Primary Acetate. The second step is the hydrolysis of primary acetate into secondary acetate. In this operation a solution of primary acetate in strong acetic acid is partially diluted with water, and allowed to stand for some time at increased temperatures, during which time the primary acetate is partially saponified (hydrolyzed) to the secondary or acetone-soluble state whose acetyl content approximates the secondary acetate.

When the reaction has reached the desired stage, the secondary acetate is precipitated by pouring the solution into a large tank of cold water. Secondary acetate is precipitated out in the form of white flakes. These acetate flakes are washed in warm water until free of acid, dried, and then stored in bins.

Spinning Solution Preparation. The spinning solution is prepared by dissolving these cellulose acetate flakes in acetone. The preparation of this spinning solution is done in a closed mixer into which the cellulose acetate flakes and the acetone are added in the proper proportions and gradually mixed together. From 12 to 24 hours are required to dissolve the cellulose acetate completely. In the final spinning solution the cellulose acetate content may range from 15 to 30 per cent. For dull luster yarns a small amount of titanium dioxide is introduced into the solution during the mixing.

From the mixer the solution is run into tanks where several batches of solution are blended. The contents of these blending tanks are then stirred several times, and finally the solution is drawn into storage tanks in which all air bubbles are removed. The solution then is ready for spinning.

Spinning Acetate Yarn. Acetate yarn is spun by the dry spinning method as contrasted with the wet spinning system used in the viscose and cuprammonium processes of yarn manufacture. In this dry method of spinning, the spinning solution is delivered from storage tanks to the spinneret on the spinning machine, through which the solution is forced under controlled pressures into an enclosed spinning chamber. The spinning solution emerging from the spinneret is met by a rising current of warm air which evaporates the acetone. By the time the acetate filaments have reached the bottom of the spinning chamber, coagulation has been completed and the filaments dried. From a chemical standpoint, the spinning is now completed. It is only necessary to twist the filaments and wind the yarn for shipment, or, if staple fiber is being made, to cut the filaments to the desired lengths, bale and ship.

Raw Materials Used. In producing a pound of acetate rayon the pounds of raw materials required are approximately as follows: Refined cotton linter, 0.70; acetic anhydride, 2.40; glacial acetic acid, 6.00; sulfuric acid,

0.07; acetone, 4.00; titanium dioxide, 0.02; as well as about a thousand gallons of water.

These figures represent gross consumption and do not take into account the recovery of any of the chemicals used. Because of the initial high cost of the chemicals consumed by this process, efficient recovery systems have been developed without which this process would be commercially and economically impracticable. It is because of the development of more efficient recovery systems for such chemicals as acetone and acetic acid that the price of acetate rayon to the consumer has been constantly lowered in the years.

Cuprammonium Process

The cuprammonium process of rayon yarn manufacture is the most common method of production. The quantity of yarn produced by this process in the United States today is small by comparison with the output of the viscose and acetate processes. This process of manufacture has, nevertheless, become an important factor in the rayon yarn industry in this country since the late war.

In this process of manufacture, purified cotton linters are commonly used as the principal source of cellulose, although in recent years this process has been experimenting with special grades of high-alpha wood pulp. In the processing, the purified cotton linters are cleaned by cooking in a mild alkali solution under pressure and then are bleached. These linters, then nearly 100 per cent pure alpha-cellulose, are mixed with basic copper carbonate and ammonia aqua of 28 per cent ammonia. This solution must be prepared under rigid chemical control to obtain a solution of the proper viscosity and cellulose content. The solution is then filtered and stored in tanks.

The solution, when used, is carried to the spinning machines and extruded by the stretch spinning device. By this method, the spinning solution is pumped through spinnerets into a glass funnel through which deionized water flows. On the way through this funnel the single filaments are stretched and slowly solidified, the water meanwhile extracting most of the ammonia and part of the copper. On leaving the funnel, the filaments pass through a bath of mild sulfuric acid which fully coagulates the filaments and at the same time extracts more of the remaining copper. The filaments are then wound on reels in the form of skeins. These skeins are sprinkled with plain water, removing any of the remaining acid and copper sulfate, after which the yarn is washed in a soap bath, dried, and then treated with a second soap bath to soften up the yarn, and dried again. The yarn is packaged on cones, bobbins, or any other form desired and shipped to customers.

The importance of these various processes of yarn manufacture in the United States is shown in the following table for selected recent years.

TABLE 49.—U. S. yarn production by process of manufacture.

	Viscose plus Cuprammonium		Acetate		Total
	(pounds)	(%)	(pounds)	(%)	(pounds)
1939	231,283	70.4	97,342	29.6	328,625
1940	257,124	65.9	132,947	34.1	390,072
1941	287,459	63.7	163,745	36.3	451,204

the rayon yarn industry in the United States has reached an impressive level as indicated by these figures.

Rayon Staple Fiber

Rayon staple fiber has been one of the outstanding developments in the textile industry especially over the past decade. Although this rayon staple fiber was originally developed in Germany during the war of 1914-18, it was not until the late twenties that appreciable progress was made. Since that time, however, its growth has been extremely rapid. In 1929 world rayon staple fiber production amounted to a little over 7 million pounds; by 1940 world production totaled 1237 million pounds. Of this 1940 world output Germany produced 575 million pounds, Japan 300 million pounds, Italy 225 million pounds, United States 81 million pounds, and all other countries 56 million pounds.

As has been previously pointed out, rayon filament yarn is composed of a number of fine, continuous rayon filaments grouped and lightly twisted together. On the other hand, rayon staple fiber is made by cutting continuous rayon filaments into short lengths. These short fibers are baled by the rayon fiber producer and shipped to cotton, woolen, worsted, or silk spinners to be spun into a yarn commonly known as spun rayon yarn.

Methods of Manufacture. Rayon staple fiber is made principally by the wet process, although increasing amounts are being manufactured by the dry process. In the production of staple fiber the chemical stages in the manufacturing process are essentially the same as those for filament yarn, as previously described; that is, the raw cellulose material is chemically treated in such a way as to put the cellulose into a solution for spinning filaments.

In the viscose process of manufacture the difference between filament and staple fiber production takes place at the spinning and not at the chemical preparation stage, as noted. As previously brought out in this chapter, in the spinning of rayon yarn the filaments are collected on bobbins, centrifugal pots and periodically doffed. In the manufacture of staple fiber these operations do not exist. Instead, the filaments from each spinneret are carried along to the end of the spinning machine to form a continuous tow or rope of filaments. Moreover, in comparison with the relatively small number of holes in the spinneret used in the spinning of filament yarn, the number of orifices in the staple spinneret is substantially greater.

This tow, however, requires additional processing before it reaches the finished state. It may be immediately cut to the desired staple lengths and frequently washed, desulfurized, bleached, and dried; or the tow itself may be sulfurized, washed, bleached, and dried before being cut into staple lengths. The former system of cutting these filaments into staple lengths is called the wet cut system, and the latter the dry cut system. Regardless of the method of cutting, however, these short fibers in their final finished state are called **rayon staple fiber**. They are then baled and shipped to the customer.

Otherwise, in the acetate process of staple fiber production, the chemical

preparation is the same as that for the continuous filament acetate. Unlike the viscose process, however, it is possible to produce acetate on continuous filament acetate yarn spinning equipment, although acetate staple is also produced on specially developed rayon staple fiber spinning machines. The acetate filaments are likewise cut into short lengths sold to textile spinners for spinning into yarn.

Types of Staple Fiber. Inasmuch as rayon staple fiber must be spun into yarn by the cotton, wool, worsted, and schappe (spun silk) systems of yarn spinning, it is necessary for rayon producers to supply this fiber in suitable lengths. Therefore, rayon producers cut rayon tow into suitable lengths as determined by the system of yarn spinning for which the fiber is intended. For the cotton system the fibers are generally cut $1\frac{1}{4}$ to 2 inches long. Lengths of about 3 to 4 inches are usually required by the woolen system, and lengths of 5 inches and over are used by the worsted and schappe spinning systems.

Similarly the denier range of the individual filaments may be varied by the rayon producer according to the customer's needs. The commercial range, at present, is from $1\frac{1}{4}$ to 20 denier per filament. Staple fiber is available in both bright and dull lusters.

The principal consumer textile products made of spun rayon yarn are apparel fabrics for men's and women's wear. This rayon product also finds growing markets in such household products as blankets, rugs, drapes, diapers, etc. The current prices of viscose and acetate staple fibers are 41 and 43 cents per pound respectively for the basic grades.

Aside from rayon yarn and rayon staple fiber, there are two other important products made by the rayon industry. These are bands and strips of rayon less than one inch wide and monofilaments of rayon. In the classification of narrow bands and strips may be included the item of artificial straw. In the monofilament category are included those single filaments of rayon filaments spun from a circular orifice. This product is often referred to as artificial horsehair. The major user of these bands, strips and monofilaments is the millinery industry.

An *artificial wool* is made by dissolving casein in alkali, forcing the solution through large-holed spinnerets, and coagulating the threads in an acid bath; Lanital, Aratex.

NYLON

Nylon yarn is a new synthetic fiber now available in commercial quantities; it comes closer to silk in constitution and properties than any other synthetic fiber previously manufactured. In 1942, the third year of its commercial availability, the annual production will reach 16 million pounds. Nylon is already well known to the general public because it has gone into considerable volume of nylon hose and other articles of wearing apparel.

Nylon is a generic name applied to all superpolymers made from long-chain amino acids or from long-chain dibasic acids combined with diamines. Nylon 66 is the specific nylon now made on a large scale; it is the superpolymer formed by the combination of adipic acid and hexamethylenediamine. These two substances, both solids at room temperature, are dissolved in solution to form nylon salt. Stabilizing agents are added to the

ular weight and viscosity; the solution is evaporated, and the liquid is transferred to an autoclave in which it is heated for many hours. The product is a melt, consisting of the final superpolymer. The melt is fed in ribbon form onto a chilled wheel (casting wheel); the cooled ribbon, now a tough, horny material, is cut into small chips convenient for storage. To make the fiber, the chips are melted by passing them over heated grids; the liquid is fed to a pump and is supplied under the pressure of the pump to spinnerets, which form the filaments. The latter are cooled at once by a gentle blast of air, and wound on bobbins. Next, the primary filaments, rather useless in their existing form, are cold-drawn



FIGURE 148.—The molten polymer is extruded from the autoclave onto a chilled wheel, the casting wheel here shown, forming a wide ribbon. A spray of water helps the mass to solidify. Nylon at this point resembles ivory. In later operations it is chopped, melted and extruded as filaments. (Courtesy of E. I. du Pont de Nemours and Co., Nylon Division, Wilmington, Del.)

to four times their original lengths, with a decrease in diameter. By this operation, their properties are changed completely, for now they form fibers, transparent, lustrous, and of high tensile strength. The reason for the change is that the original random arrangement of the polymer molecules gives place to an oriented one. The cold-drawn filaments are twisted, sized, and rewound on spools or cones, ready for the mill.

Nylon fiber may be made into any of the standard deniers. The diameter of the individual filaments is governed by controlling the rate at which the molten nylon is pumped to the spinneret, and by the rate at which the filaments are drawn away. The filaments from one spinneret are united

to form the yarn; the number of filaments in the yarn is determined by the number of holes in the spinneret. Filaments of extreme fineness can be made from nylon, much finer than those of ordinary textile fibers.

Nylon may be delustered as rayon is, by the addition of finely powdered (colloidal) titanium dioxide or similar pigments. Nylon may be dyed in the molten mass, or the yarn or finished fabrics may be dyed, preferably with acetate rayon dyes.

Nylon textile monofilaments are comparatively thick single filaments which serve for making supersheer hosiery, insect screening, and for other purposes. Nylon solutions permit the coating of metal wires for insulation. Nylon molding powder is being developed for injection-molding equipment. Nylon fiber is used for shroud lines and canopies for parachutes, and for other military purposes.



FIGURE 149.—Spinning the nylon yarn: the extrusion of molten nylon through a spinneret to form the filaments which become solid as soon as cool air strikes them. (Courtesy E. I. du Pont de Nemours and Co., Nylon Division, Wilmington, Del.)

Nylon is not soluble in water, nor in most of the ordinary organic solvents; it dissolves in phenol, cresol, and formic acid. The filaments may be dry-spun with such a solution, as acetate rayon is, but because of the nature of the solvents this is not desirable.

Nylon 66 melts at 263°C . (511°F .). The tensile strength is 4.3 grams per denier, dry, 4.0 to 6 grams, wet, depending on degree of molecular orientation and chain length; for comparison, a good silk has a tensile strength of 4.5 grams dry, and 3.8 grams wet.

The two raw materials for nylon 66 had to be manufactured by special processes, for until this development, adipic acid and hexamethylene diamine were not made commercially in this country. Adipic acid, $\text{COOH} \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{COOH}$, is made from phenol. First, the phenol is hydrogenated to cyclohexanol, with the aid of a contact catalyst.

temperatures. Next the cyclohexanol is oxidized, also catalytically, to adipic anhydride, which is readily hydrated to the acid. Hexamethylenediamine is made from adipic acid by treating it catalytically with NH_3 to form the dinitrile, and hydrogenating the latter to give the final product, $\text{NH}_2 \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{NH}_2$, a solid at room temperature.

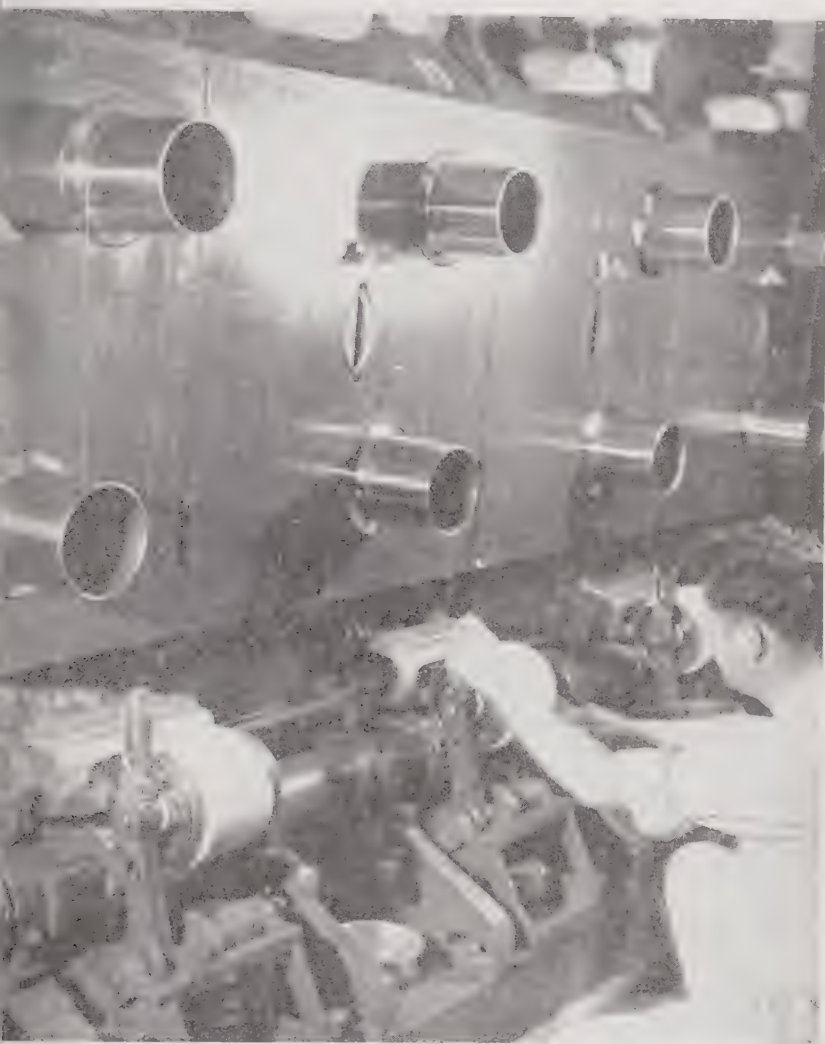


FIGURE 150—Nylon yarn, formed by bringing together the fine filaments extruded from the spinneret, is wound on bobbins and sent on to the textile area of the plant where it is given various treatments similar to those accorded other fine yarns. (Courtesy E. I. du Pont de Nemours and Company, Nylon Division, Wilmington, Del.)

The linear polymer forms by the combination of the end group of the acid with the end group of the diamine, leaving at each end of the new polymer molecules reactive groups which undergo similar combinations. The first molecule would be $\text{COOH} \cdot (\text{CH}_2)_4 \cdot \text{CO} \cdot \text{NH} \cdot (\text{CH}_2)_6 \cdot \text{NH}_2$.

CELLOPHANE, SEALING CAPS, CELLULOSE SPONGE

Transparent paper (Cellophane, Transparit, Sylphrap) is made by extruding a viscose solution through a long narrow slit into a setting bath. Kodapak is a cellulose acetate sheet of high transparency. The size of the slit determines the thickness the paper will have; the length of the slit also determines the width of the paper. The process is continuous, and a sheet of any length is produced. It passes through the setting bath, through which to remove acid, through a bicarbonate solution to neutralize the last bath of acid, through a soda ash solution to remove sulfur, through a dilute solution to remove the carbonate, through water, then through a glycerin solution from which is absorbed 17 per cent glycerin. It is then dried on rollers and drums and rolled, very much as paper is (Chapter 21). The transparent paper may be colored by passing the paper in the gel state, that is, after alkali and acid removal, through a dye solution. It may be embossed by passing it between engraved copper rolls.

Cellophane is made moisture-proof and water-proof by passing the sheet after the glycerin bath, through a bath consisting of a dilute lacquer solution with rather volatile solvents such as ethyl acetate. The sheet in this form continues to a chamber wherein warm air removes the solvent. The lacquer with the proper amount of plasticizer and softeners remains as a coating. The solvents are recovered by means of activated carbon.

An artificial sausage casing has been for some time successfully marketed; it is seamless, and is made in the same way as transparent paper.

Hydrated cellulose and cellulose acetate may be formed into caps for sealing bottles. The caps are kept under water until needed. In order to apply a cap, it is placed loosely over the stoppered neck of the bottle and left over night. It shrinks and attaches itself firmly to the neck of the bottle, sealing it.

Cellulose Sponge. A strong, durable sponge is made from viscose by incorporating Glauber salt crystals of all sizes, placing boxes with the viscose in the coagulating bath, and precipitating the cellulose. Some other fibrous material may be mixed with the viscose. The blocks so formed are leached with warm water, removing the crystals, which leave corresponding cavities. An improvement^{8a} consists in coagulating with a hot salt solution, which penetrates quickly into the interior of the blocks, and also causes the contained Glauber salt to melt and thus be simultaneously removed. The blocks are cut into square-edged pieces about right for one's hand. They take up water and may be squeezed from it just like a sponge. A cellulose sponge with uniformly fine cells is made by using fine crystals exclusively.

VULCANIZED FIBER⁹

Vulcanized fiber is made from cotton and linen rags, not from cellulose. The rags are washed, shredded in a beater engine and made

⁸ Visking Corporation, 4311 Justine Street, Chicago, Ill.

^{8a} U. S. Patent 1,909,629, to Hugo Pfannenstiel; earlier patents are 1,142,619 and 1,611,056.

⁹ Description written specially for this text by Dr. Gustavus J. Esselen, Cellulose expert, Mass.

in the same way as explained in Chapter 21. The paper is then passed through a solution of zinc chloride of approximately 70° Bé. concentration. This gelatinizes the paper and permits it to form a homogeneous sheet in the following operation, which consists in winding it on a heated roller until the desired thickness has been reached. It is then washed in successive solutions of gradually decreasing zinc chloride content, and finally with water. The washing operation is a time-consuming one and takes anywhere from ten days to two months, depending upon the quantity of the stock. After the zinc chloride has been completely removed, the vulcanized fiber is dried, and is then subjected to a preliminary flattening operation, following which it is calendered by passing it through heavy rolls.

Although the larger part of the vulcanized fiber is now made by the zinc chloride process described above, there is still a certain amount made with sulfuric acid in which a cold acid of about 54° or 55° Bé. concentration is used. With this process, the paper is not ordinarily wound on a forming machine but several layers are passed through the acid simultaneously and are then dried by running them between a pair of rollers under pressure. The finished sheet is run through dilute sulfuric acid and finally washed in water.

Vulcanized fiber is unusually tough and resistant to abrasion, yet it can be easily worked by mechanical means. It finds extensive use for containers such as wardrobe trunks, roller trucks in textile mills, waste baskets, etc., where the material has to withstand hard usage for long periods of time. Its chief drawback is the fact that it absorbs moisture and therefore does not hold its dimensions accurately under changes in atmospheric conditions. For example, if immersed in water for 24 hours, it will absorb between 40 and 60 per cent of its weight of water, and swell considerably in the same time.

The usual color of vulcanized fiber is gray, although it can be readily dyed in red, black or other colors by the introduction of suitable pigments during the process of making the paper.

OTHER PATENTS

U. S. Patent 1,839,773, manufacture of rayon, by aging soda cellulose from wood pulp, converting to cellulose xanthate; 1,790,599, spinning of artificial silk, cellulose especially; 1,770,750, manufacture of artificial silk thread by cellulose process; 2,012,723, spinning viscose by centrifugal, and washing in spinning box (Al) with a hot solution of the salt of a weak acid, with alkaline reaction; 1,702,837, rayon process; 1,756,435, treating rayon to remove detrimental chemicals; 1,871,245, process for making viscose, to serve for rayon and cellophane; 1,841,420, in viscose solution, H₂S liberation prevented by converting the S compounds into non-toxic ones; 1,811,512-3, shortening the time of ripening of viscose by adding hemiacetals at some stage of the preparation; 1,779,521, viscose, forming a soluble acetate, and removing S compounds before precipitating the viscose; 1,790,990, method of obtaining viscose from cellulose; 1,990,556, on a rubber funnel thread guide; 2,060,964, apparatus for spinning rayon; 1,984,853 and 1,986,813, apparatus for spinning rayon; 2,012,723, production of artificial filaments; British Patent 417,920, on artificial products of viscose; U. S. Patents 1,993,816 and 1,990,617, apparatus for making rayon; 2,012,723 and 2,012,723 on rayon manufacture; 2,018,028, 2,010,822, 1,995,732, 2,022,856, method of making cellulose acetate; 2,020,247, cellulose acetate composition and plasticizer; 2,012,723, making cellulose esters; 1,990,113, apparatus for manufacture of cellulose acetate; 2,279,771, nylon, to insulate and coat electrical wires.

PROBLEMS

1. 100 pounds of cotton linters which contain 98 per cent α -cellulose are made into viscose. The batch is treated with 15 per cent NaOH to produce the cellulose and the latter is churned with 46 pounds of CS_2 . Make an estimate of how much xanthate is formed, using the formula in the text for your composition. This is spun, and the yield in the form of filaments in thread form is 88 per cent. What is the weight of rayon obtained?

2. For a daily capacity of 10 tons of product, what volume of viscose with 96 per cent cellulose must be handled, the recovery in this case being taken as 96 per cent. What is the number of tanks you must have ready filled with the viscose for a day's supply, for the production just stated? The tanks are upright cylinders, 6 feet in diameter and 10 feet high. The specific gravity of the viscose is 1.11 at 64° F.

3. Sixteen times the original 125 pounds of sulfite pulp, with a content of 80 per cent α -cellulose, 2 per cent β -cellulose, and 6 per cent hemi-cellulose have been made into a viscose with 6.7 per cent cellulose in solution. This viscose also contains 6 per cent NaOH. In spinning this amount, there will be neutralized in the spinning bath how much sulfuric acid? And what is the weight of sodium sulfate? Glauber salt which must be removed in order to discard the exact increment of salt by the neutralization process?

4. Let all of the cellulose in the viscose, as per Problem 3, be made into cellophane, without loss. What will be the weight of the cellophane obtained, allowing a 17 per cent glycerine content, and a 3.5 per cent residual moisture?

5. A batch of cellulose acetate yarn is manufactured, the cellulose acetate corresponding to 240 pounds of cellulose in suitable form. Using the quantity relationship in the text, how much acetate yarn will be obtained, assuming no loss and no waste?

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The three foods essential to the well-being of man are proteins, fats and carbohydrates; the most palatable form of the latter, sugar, found in nature and needs only to be extracted from the plant. Another form is starch, found in a still greater number of plants, and usually extracted for food purposes; it is isolated for industrial purposes from it, among other things, an artificial sugar is made, which is a

Chapter 23

Cane Sugar, Beet Sugar, Corn Starch and Glucose

The extraction of sugar from the plant, and the refining of the extract, are important industries, for sugar is a favorite and practically universal food. It is estimated that the average man in the United States consumes two pounds of sugar per week. The white, crystalline substance which is usually called sugar, is more correctly designated as sucrose or disaccharide. The plants in which it occurs, and which are used as sources are the sugar cane* and the sugar beet; the former grows in tropical countries, the latter in temperate ones. The method of extraction from the cane is to crush the cane and collect the juice which forms; it is essential to press the canes as soon as cut, for otherwise there is an inversion of sucrose to invert sugar, which represents a loss of crystal sugar. The juice must be concentrated and crystallized in the neighborhood of the plant, for it contains much water which could not be transported without shipping expense. It is customary therefore to work up the cane juice into a first-crystallized sugar in many rather small plants. As this first sugar is still colored, and has an unpleasant odor, it must be refined; this is done in a few central plants, the refineries. Hence it is well to distinguish three industries, cane sugar manufacture, cane sugar refining, and beet sugar manufacture; the last is so conducted that no refining is required. It should be remembered that although the word "manufacture" is used, there is really no manufacture of the sugar, but merely an extraction; the sucrose is already present as such in the sugar cane or beet.

The relative importance of the various sources for sugar in the United States is indicated in Table 50.

Over half of the world's supply of cane sugar is obtained from Cuba, the greatest cane sugar-producing country; the next in importance is Java, whose product normally provides Great Britain with a part of its needs. In the world production, two thirds are cane, one third is beet sugar. Before the war of 1914-18, the production of beet sugar was greater, but during that war it fell off, since Germany, and France and Belgium next, were the greatest beet sugar producers. The beet sugar industry is gradually regaining its place. Within the United States more beet sugar is produced than cane sugar; the latter comes mainly from Louisiana. The neighboring southern states raise a small crop of sugar cane which is made into sugar.

* The sugar cane originated in India, and was known to the Greeks and later to the Romans. It spread from there, by the agency of man, in succession, to China, Arabia, Persia, Morocco, the Azores, Cape Verde Islands, island of St. Thomas, Brazil, Jamaica (1656), San Domingo (1687), and experienced the first blooming of its cane cultivation in 1772, although the introduction had taken many years before; the cane was brought to Louisiana in 1751; it was also carried to Java at about the same time.

TABLE 50.—Sources of sugar (sucrose).*

	1939 Short tons	1940 Short tons	1941† Short tons
production			
sugar	12,495,000	13,123,000	
sugar	23,044,000	22,185,000	
el	35,539,000	35,308,000	
tion in Cuba (cane)	3,156,845	2,733,910	3,400,000
record: 5,894,170 in 1924)			
ental U. S. production			
sugar	504,000	332,000	431,000
sugar	1,758,000	1,897,000	1,553,000
ts into U. S. from Cuba			
sugar (cane)	1,588,965	1,839,223	
ed sugar (cane)	343,496		
tion in Philippines (cane)	1,141,841	1,282,440	1,100,000
to Rico (cane)	1,018,803	931,997	1,170,000
aii (cane)	976,677	1,000,000	1,000,000
in Islands (cane)	7,236	8,400	9,000
tion in Brazil (cane)	1,296,000	1,425,000	
ntina (cane)	574,000	593,000	
(cane)	522,000	504,000	
uth American total	2,720,000	2,878,000	
(cane)	1,769,000	1,960,000	
ralia (cane)	1,045,000	905,000	
n South Africa (cane)	596,000	573,000	
sugar production			
ia	2,923,000	2,968,000	
t Britain	591,000	583,000	
len	343,000	331,000	
many	2,196,000	2,515,000	
hoslovakia	651,000	838,000	
nd	520,000	640,000	
	527,000	600,000	
is countries total	4,566,000	5,395,000	
ce	1,102,000	550,000	
occupied countries	1,933,000	1,421,000	

assembled from figures supplied by the Division of Statistical and Historical Research, Bureau of Cultural Economics, Department of Agriculture. Estimated.

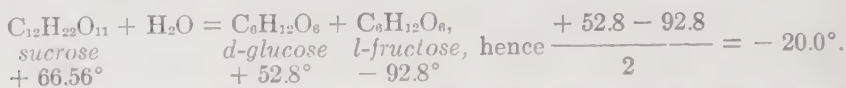
The growth of the beet sugar industry, in competition with imported sugar, has been steady, thanks in part to a protective tariff of $\frac{1}{2}$ to 2 a pound,¹ in part to modern equipment and scientific studies of the use of the beet.

The shortage of sugar in the United States in 1942 is due in large part to the loss of the Philippine crop.

In the evaluation of sugar, the fact is utilized that sucrose dissolved in water rotates the plane of polarized light to the right; the invert sugar is formed from sucrose by the action of certain organisms or of acids which rotate the plane of polarized light to the left; other impurities have no effect.

The tariff for 75° sugar was 1.7125 cents per pound, with 0.0375 cent more for each additional degree above 75°. The U. S. Tariff Act of June 18, 1930. Cuban sugar is 96°, hence should pay 2.50 cents per pound. A 20 per cent preferential is applied, however, so it paid 2 cents. In the U. S. Tariff known as the Flexible Tariff, of June 8, 1934, the duty was reduced; it has been changed by supplementary legislation several times since then, both ways. The rate now in force is in the agreement of January 1, 1942, which provides, for Cuban sugar, a duty of 0.51375 cent per pound of 75° sugar, 0.01125 cent for each degree, making 0.75 cent for 96° sugar. Other foreign sugars pay 1.875 cents per pound for 60° grades. The degree of sugar is obtained by reading the rotation of a beam of polarized light. The rotation is proportional to the amount of cane sugar present. In "direct polarization" the instrument is so arranged, and the amounts of sample and solvents are so chosen, that the reading is also the percentage of sucrose, without any further calculation.

effect on the polarized beam. Hence the extent of the rotation to the right is a measure of the sucrose content of any solution, or of any solid substance, by dissolving it. The instrument used is the polariscope, or if the readings are marked directly in percentage of sucrose, the saccharimeter. The polariscope is the more common, and is conspicuous in any sugar laboratory. The reaction for sugar inversion with the degrees of rotation for the substances in each case, and the direction of rotation (+ for right or dextro, - for left or levo) is:



The sum of the rotation of the two mono-saccharides, on the right of equality sign, is a negative rotation, hence there is an inversion of the sign. Glucose and fructose are sometimes called reducing sugars, because they reduce Fehling's solution, whereas sucrose does not.



FIGURE 151.—Front view of a sugar cane crushing mill. (Courtesy of Geo. L. Squier Manufacturing Co., Buffalo, N. Y.)

² The polariscope is a half-shadow instrument whose original form is due to Antoine Laurent Lavoisier. Compare the "Chemical Dictionary," 1924, or more recent editions, by Dr. Walter Roth, published by J. Springer, Berlin, or other chemists' handbooks.

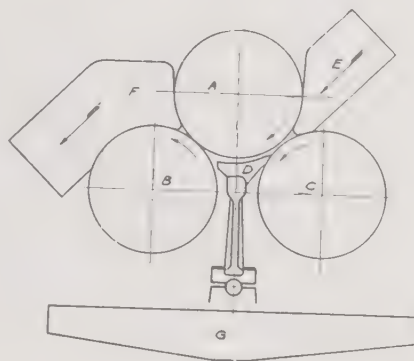
³ The name invert sugar is due to this inversion of the sign of rotation.

SUGAR FROM THE CANE

The sugar cane is a species of grass, with a single, woody stalk, surmounted by a group of broad leaves; it reaches a height of 18 feet, and is raised from cuttings of specially grown canes called the seed canes. At maturity, the plant develops many very small flowers at the top, forming a panicle. In harvesting, the cane is cut at the ground, the leaves and tuft are removed, and the stalk only carried to the mill. Because of the danger of fire, the cane must reach the crushers in a few hours, so that a mill is usually only a limited territory. The sucrose content in the sugar cane varies between 16 and 20 per cent of the total weight.

At the mill (Fig. 151) the canes are first cut into short pieces by the cutting knives, and then pass to one or more three-roller crushers, where the juice is pressed out. The rolls revolve slowly, and are arranged in corrugations. In the usual form, one roll surmounts the lower two. The cane travels as indicated in Fig. 152, and is carried from one lower roller to the second by the trash plate. If no water is added, the cane is said to be dry-crushed; if water is played on the cane at the second or third set of rollers, it is wet-crushed. The pressed cane is the "bagasse," which is used further. The juice drops into troughs under the rollers and is

FIGURE 152.—Crushing rolls for sugar cane, with typical turn plate arrangement. *A*, top-roller; *B*, feed roller; *C*, bagasse roller; *D*, trash plate; *E*, feed of cane; *F*, discharge of crushed cane. The juice runs off at *G*. (Special drawing prepared by Geo. L. Squier Manufacturing Co., Buffalo, N. Y.)



ed, warmed to 200° F. (93° C.) and run into settling tanks for a short

time. The bagasse still retains some sugar; in some plants, it is passed through a low trough containing water, on an endless belt, and pressed in crushers once more. The dilute solution so obtained may be added to the juice. The spent bagasse is a sponge-like material; it serves as fuel, sometimes with the addition of crude oil, or fuel oil; as a source of cellulose; or making Celotex board.

The amount of juice in the cane varies in different territories; it varies with the degree of maturity. Of the juice in the cane, 60 to 80 per cent is extracted, depending on the perfection of the equipment. An analysis of the juice follows⁴:

⁴After Spencer, quoted from U. S. Dept. Agr. Farmers' Bull. 429, 15 (1911).

	Per cent
Water	83.6
Sucrose	14.1
Reducing sugars6
Undetermined solids	1.7
Total	100.0

Defecation. After any coarse material has settled out, the juice, which is still turbid, and has an acid reaction, is drawn into mixing tanks and treated with enough lime to render it slightly alkaline. The lime precipitates a number of undesirable impurities; the limed juice is warmed by steam, and the precipitate forms a crust (1 hour); the albuminous material coagulates on the lime precipitate and is carried down (or up) with it. After



FIGURE 153.—A quadruple-effect evaporator, installed in a Puerto Rico sugar plant (Courtesy of the Geo. L. Squier Manufacturing Co., Buffalo, N. Y.)

settling, the clear juice is drawn off to the evaporators. (See Fig. 153.) The remaining precipitate is filtered in presses of the plate or of the band and leaf type,⁵ the cake washed somewhat, and used for fertilizer.

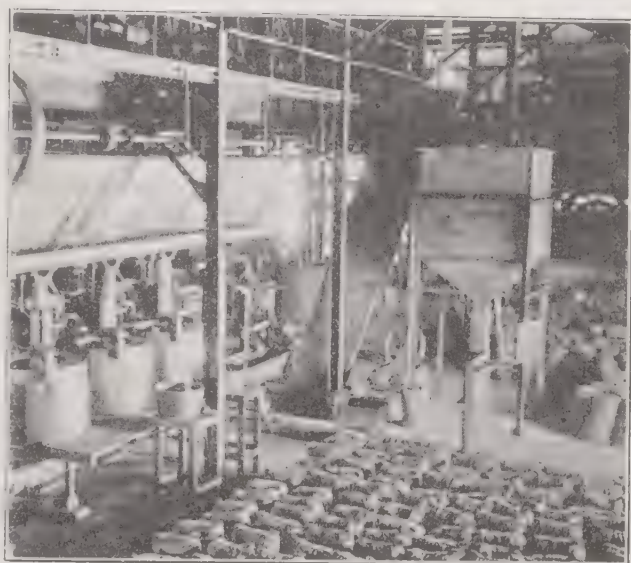
First Evaporation to a Syrup. The comparatively dilute juice, with about 14 per cent sucrose, is evaporated first to a strong solution, with about 50 per cent sucrose; such a solution is still clear, but is viscous. This evaporation is generally performed in double- or triple-effect vacuum boilers,⁶ in order to save steam.

⁵ Chapter 42.

⁶ Chapter 43.

Second Evaporation to Crystal Formation. The syrup is concentrated in a single-effect vacuum pan, in which the vacuum and steam may be regulated as the operator deems necessary. In the double-effect for the first evaporation, exhaust steam is used; for the vacuum pan in the second evaporation, boiler steam is used in numerous coils. The syrup is evaporated until a blob on a glass plate examined by lamplight glistens because of the presence of very small crystals which have formed; this is called the graining. More syrup is then added, in small portions, and the new sugar crystals grow on the crystals, causing them to grow. This is continued until the desired growth has been attained; the mass in the pan is then the "massecuite" with a total of 82 per cent sucrose, and perhaps 8 per cent water. In the total sugar, the hot massecuite has 56 per cent as crystals, 44 per cent in solution; after cooling, 65 per cent as crystals, 35 per cent in solution. The thick mass, semi-solid, is placed in centrifugal baskets,⁷ the adhering

FIGURE 154.—Interior view in a Puerto Rican sugar plant, showing the centrifugal machines, on the left, in which the raw sugar is freed from the mother liquor or molasses. This raw sugar is packed in bags for shipment to the refinery, where the white crystal sugar is prepared.



molasses is whirled off to the envelope, collected and stored as molasses (Fig. 154). The crystals are washed in the basket by clear juice, then removed by a conveyor. They constitute the raw sugar, which the refineries purchase. The molasses may be concentrated again, until it contains no more sugar that can be crystallized, when it is sold for cattle food, for the manufacture of industrial alcohol, or other purposes.

Figure 155 is shown a flow-sheet for a sugar mill making raw cane sugar; the operations lead to the main product, the raw sugar, here "A" and to a second product, "C" sugar. A by-product is the molasses. From "C" molasses, also called "blackstrap;" another by-product is the mud from the clarifier, a fertilizer; still another is the bagasse which may be burned up into Celotex or other cellulose products.

Until recently, the raw sugar mills were situated in the tropics, near the

cane fields, while the refineries were situated within the United States, operating on Cuban and West Indian sugar being mainly along the Atlantic seaboard. A change is taking place: more and more sugar is being refined in the tropics. To the raw sugar mill there is added a refinery, and the sugar leaves the country of origin in the form of refined sugar. One reason for this development is that by means of better heat balances, the raw sugar mill uses less steam, and has left great quantities of bagasse which can be utilized under a boiler to make useful steam only if a refinery is established.

CANE SUGAR REFINING

The raw cane sugar generally purchased by the refinery has 95 per cent sucrose; it contains perhaps 1 per cent of glucose, 0.5 per cent ash, and the rest moisture. The main task of the refinery is to remove the color and slight odor. The raw sugar is mixed with a mother liquor from the previous batch, which removes a large part of the color, leaving the crystals partially dissolved; these are centrifuged, washed while in the basket, and dissolved with very little hot water to a syrup. A small amount of lime is added, steam blown in; the suspension is filtered by passing it through bone-char in cylinders 20 feet high and 3 feet wide. The filtered liquor is concentrated to massecuite as was described for raw sugar, centrifuged, and dried in a rotary drier, for example, to produce granulated sugar. The whole or white massecuite may be solidified to a loaf, which may be cut into smaller cubes or flat pieces (domino sugar). There are many other modifications which lead to special forms.

The bone-char filters are used until they no longer bleach; water is then turned in to remove most of the adhering sugar, the char is dumped, and revived by heating it in absence of air to red heat; it may then be used over again. After a number of such treatments, it loses its decolorizing property and is sold for its phosphate content to the fertilizer trade.

There are simpler ways to purify the sugar; thus under favorable conditions mere mixing with a mother syrup, centrifuging, and washing the sugar solutions while in the basket, finally with steam, produces a nearly white product. On the other hand, bleaching by passing sulfur dioxide through the white syrup after addition of lime is also practiced, followed by filtration through the bone-char cylinders.

The mother liquors are rather pure, and are usually made into syrups, or mixed in some cases with maple syrup.

Other methods for bleaching and refining: The greater part of the sugar refined in continental United States is still bleached by means of bone-char, yet this method faces a decline, probably a rapid one, for it is often difficult to provide the bone, especially in the tropics. One of the new methods especially adapted to the tropics makes use of Suchar, a coconut char which is used once and thrown away. Other similar chars are Norit and Deccan. Another very successful method is Sucroblanc, in which the procedure is as follows: The raw sugar is first "washed," by making it into a mash with green liquor or other sugar liquor, and hydroextracting it in centrifuges. The resulting "affinated sugar" is dissolved in hot water to 60 or 65 per cent, and 0.1 to 0.3 per cent of the reagent Sucroblanc stirred in at room temperature.

WEIGHING AND FEED APPARATUS

KNIVES OR SHREDDERS

CRUSHERS AND MILLS

FIBER (Bagasse)

To boilers as fuel, or
To balers for use in
Cellulose by-product plant

PLANTS

SCALES

G APPARATUS (Sulfuring apparatus if plantation white sugar being made. Other flocculating agents added here when composition of juice requires.)

HEATERS (Exchangers)

FLOCCULATORS OR CLARIFIERS

Continuous type with
sludge propulsion

"Dorr" single or
double clarifiers
(OR)
"Seip (Graver)" Clarifiers
(OR)
"Rivers Fortier" Clarifiers

RAW JUICE

(SLUDGE)

(Mixed with bagacillo to
form filtering medium)

Rotary Oliver
or
Campbell Filter
Filter Presses

Clear Juice

Muds

To potash burners or direct to open pits in fields
for fertilizer use.

MULTIPLE-EFFECT EVAPORATORS (Triple- or quadruple-effect evaporators)

2)

STORAGE TANKS (For syrup and molasses storage)

HEATING PANS (Single effect evaporators arranged for careful operating control as
to temperature and pressure.)

CRYSTAL FORMATION (MASSECUITE) (A brown dough-like mass)

CRYSTALLIZERS (Water cooled types with rotating cooling elements or LaFeuille
crystallizer—Rotary type.)

STIRRING IN MIXING TANK (To reduce viscosity of mother liquor)

CENTRIFUGALS

{ High-speed centrifugals—1800 to 2000 rpm. used on sugars with high
viscosity of mother liquor or molasses
Low-speed centrifugals—1200 rpm. or less used on "A" sugars

RAW SUGAR "A" MOLASSES

"A" Molasses mixed with fresh syrup, and
"C" Sugar boiled to make "B" massecuite (in vacuum pans) ←

Vacuum Pans

Centrifugals

"B" Sugar
Crystals washed
in centrifugals

"B" Molasses

Mixed with fresh syrup and boiled (in vac.
pans) a 3rd time to make "C" massecuite

Vacuum Pans

Centrifugals

"C" Molasses (Blackstrap)
Final to distillery or other
by-product use

"C" Sugar

Pol.
ar, ready
ry

FIGURE 155.—Flow Sheet for a Sugar Mill, Making Raw Cane Sugar.

ture or slightly higher. The reagent contains high-test calcium hypochlorite, such as Perchloron, calcium superphosphate, lime and Filtercel. The slight gas evolution (oxygen) which causes the colloidal impurities to rise to the top of the solution; the clear, decolorized sugar solution may be poured off from the bottom. Thus two steps in the older process, defecation and bleaching, are here performed in one. The clear sugar solution goes to the evaporator and strike pan to make crystal sugar.*

SUGAR FROM THE SUGAR BEET

Within the United States, Michigan, Utah, Colorado, and coastal California are the main producers of beet sugar.⁸ Thanks to the efforts of European scientists a strain of beets has been developed which produces beets containing as high as 18 per cent sucrose, rivaling the sugar cane.

At harvest time, the beet root, free from the leaves, is carted to the house, washed free from dirt, and cut into V-shaped slices about one-quarter of an inch in thickness; these are the "cosettes" or noodles. They are arranged in a number of diffusion vessels, so arranged that the noodles may be delivered to any one of the 20 or more vessels from one overhead spout. The extraction is by hot water, in contact with the slices, on the countercurrent principle. Hot water enters the diffuser whose charge is nearly exhausted; sugar diffuses from the cells of the beet into the water; the solution then passes to the next diffuser, whose slices are richer. The solution leaving the last diffuser was in contact with a fresh charge. In this way the solution is strengthened until it contains about 12 per cent sucrose, forming a thick solution. The exhausted noodles are washed out of the tank to a receptacle where they dry and are carted away to farms, to serve as cattle feed.

The warm diffusion juice is agitated with 2 to 3 per cent of lime for 24 hours, after which carbon dioxide is passed in to saturation. The precipitate which forms carries down nearly all impurities; the juice is filter-pressed and in some plants is treated with lime followed by carbon dioxide a second time, and even a third time. The filtrate obtained is pale yellow; most of this color is removed by sulfur dioxide, which also decomposes some of the calcium with organic acids, precipitating calcium sulfite. As a rule sulfur dioxide treatment follows the first lime treatment. The filtered solution is ready for the evaporators is purer than the corresponding solution from the sugar cane. The concentration is performed in double- or triple-effect evaporators, to a clear syrup, as for cane juice, and this is followed by graining in the vacuum pan. The crystals separated by centrifuging are washed in the basket, and after drying, are ready for the market. The mother syrup is concentrated again, giving crystals which are re-washed and a mother liquor, the molasses. As much sugar as possible is crystallized from the molasses as possible; the remaining sugar is recovered by a chemical process to give finally crystal sugar for the greater part. In other factories the molasses is sold as such for consumption. Beet sugar molasses is also used for making industrial alcohol.

* U. S. Patents 1,989,156; 2,091,690. Compare also "Modern Sugar Refining," *Chem. Met. Eng.* 119 (1942).

⁸ The main producing countries are listed in the introduction. There might be added Czechoslovakia, the Kief region in Russia, and central Italy.

The sugar in the molasses may be recovered by diluting to about 7 per cent sugar, cooling to 12° C. (53.6° F.), and adding pulverized lime from a nond type mill⁹ while agitating violently; tricalcium saccharate precipitates. It is filter-pressed and washed and serves instead of lime in the clarification of the warm diffusion juice (Steffen process). When this process is used, the total recovery of sucrose in the beet is 85 to 88 per cent. There is still sugar left in the mother liquor from the Steffen process; it may be recovered by means of the barium saccharate process, successfully adopted by a large American beet sugar company. Barium hydroxide is added to the discarded molasses; the sugar precipitates as monobarium saccharate, which is filtered, and decomposed by means of carbon dioxide. Barium carbonate and barium silicate are formed, and a solution of sugar which is worked up as usual. The barium carbonate is put through a cyclic process, for the regeneration of barium hydroxide. The carbonate is mixed with sand, or barium silicate from a previous run, and furnace-fused to form dibarium carbonate. This latter is suspended in hot water, giving a solution of barium hydroxide and monobarium silicate. The sugar produced by this process is of the highest purity.

Other forms of sugar are sorghum or sorgho syrup (Alabama), maple sugar (Vermont and New York), and honey, at one time of great importance; to these natural sugars, manufactured glucose, described in the latter part of this chapter, must be added. Another natural sugar which may be obtained in quantity at some future time is crystallized levulose from the Jerusalem Artichoke, which has been grown in Pennsylvania.¹⁰ The root contains as high as 12 per cent fructose (levulose), of which 80 to 85 per cent may be recovered in crystallized form. Glucose from starch is treated in this chapter, and "sugar by the hydrolysis of wood cellulose" is treated in Chapter 16.

CELOTEX

Instead of burning bagasse under boilers, it may be made into a building material called Celotex. The bagasse is freed from gums and waxes and the remaining pulp made into sheets one-quarter inch thick, very much as cardboard is made. After drying, the resulting board is suitable for sheathing buildings, either as outside covering or under clapboards and shingles. Stronger than wood, and has a high insulating value. A certain amount of resin clings to the cellulose.

STARCH

Starch, like sugar, occurs as such in the plant and requires only extraction. Corn is 65 per cent starch; wheat, rye, and rice contain a high percentage of starch; potatoes contain 15 per cent. If a raw potato is sliced, and the gratings gently agitated in a tumbler of water, a cloudy suspension forms which, strained from the pulp, deposits a white powder in a short time; this powder is the starch. The process of extraction in every case is essentially as given, but with a great variation of details. Starch is a food; heated with water it partly dissolves, and the solution has

⁹ Chapter 44.
¹⁰ *J. Eng. Chem.*, **16**, 1250 (1924).

adhesive properties, which leads to its use as a size. Hydrolyzed, the starch molecule $(C_6H_{10}O_5)_n$ gives dextrin or British gum, with a somewhat smaller molecule; maltose, the disaccharide, on continued hydrolysis; finally, *d*-glucose, the monosaccharide, discussed under sugar. To a great extent, all these products are formed at the same time; on lengthening the process, more dextrin passes into the lower forms; with the longest treatment, all the starch passes into *d*-glucose.¹¹ The hydrolysis is hastened by the use of dilute mineral acids, and these are therefore used for the production of commercial glucose, the syrup, from starch; for this manufacture starch extracted from the plant becomes a raw material.

Starch from Corn (Maize) and Corn Oil. In the United States, starch is made almost exclusively from corn.¹² The corn is steeped in water which contains a small amount of sulfurous acid (H_2SO_3), chiefly as a germicide; the softened grain is shredded in squirrel-cage disintegrators,¹³ and is suspended in water, with agitation. The corn seed, or germ, floats on top and is run off with a gentle flow of water from the surface of the tank; hull, starch, and gluten remain in the water and are run off at a later take-off.

The germs are rich in oil; they are collected, dried, and pressed for oil in a way very similar to the pressing of flaxseed for linseed oil¹⁴; the product is corn oil. The press cake serves as a cattle food.

The suspension containing the starch is screened through bolting cloth stretched on a frame of wood to form a cylinder, which slowly revolves about its long axis; starch and gluten pass through, the hull is retained. The starch suspension is next passed through a long shallow trough slightly inclined at the far end; the starch grains settle in the trough, while the gluten floats off. The separation is not perfect; even after repeating the process the gluten still contains a large percentage of starch. The gluten is milled into gluten meal (filter press) for special breads.

The starch in the troughs or runways is shoveled onto small cars, and is, again for certain grades, settled and dried at a low temperature.

GLUCOSE

In order to change starch to commercial glucose, the syrup, it is hydrolyzed with a 0.5 per cent sulfuric acid solution; in Europe, hydrochloric acid is generally used. The starch is suspended in much water, the acid is added in a preliminary, open converter, and the whole heated with steam; after an hour, it is transferred to the closed converter, of copper, and heated further by direct steam under a pressure of 50 pounds; the time in the second converter varies from 10 to 20 minutes. The discharged product is neutralized with soda ash; impurities separate in the neutral solution, are filtered, and the clear filtrate is passed through bone-char filters. A second filtration is followed by adjustment of the pH of the glucose syrup to 4.5 by means of a small amount of hydrochloric acid (never exceeding 0.0047

¹¹ The old name for dextro-glucose, namely dextrose, has become irrational since the synthesis of levo-glucose, and should therefore be abandoned.

¹² In 1914, 97.4 per cent of the starch made was from corn, 1.6 from potatoes, 1 from wheat. In Germany, potatoes are the usual source (U. S. Tariff Commission *Tariff Information Summary* G. 24, p. 14); in 1929, 93 per cent of the starch made was corn starch (U. S.), and in 1935, 90.7 per cent.

¹³ Chapter 44.

¹⁴ Chapter 29.

reconcentration to proper gravity, and neutralization of the mineral by sodium acetate, leaving the pH at the proper figure. This is done to prevent inversion of cane sugar when the syrup is mixed with it in confectionary manufacture. The final syrup is about 45° Bé. and is clear and ess.

Commercial glucose is not a single substance in solution, but a mixture of dextrin, maltose, and glucose. The bulk of the syrup on the market contains about 34 per cent of reducing sugar, essentially glucose, and called as such. It serves in the confectionery trade as a sweetening agent; also sold in small cans for consumption as a syrup in households.

By using more acid and heating in the closed converter for a longer time (30 minutes), the conversion to glucose is approximately complete. A solution rotates polarized light farther to the right than *d*-glucose; still in rotation has therefore become a means of following the progress of conversion. The product after neutralization and filtration may then be made into a solid, by evaporating in two steps, as with cane sugar. In the first step, the syrup is produced, and this enters a single-effect vacuum where it is concentrated to 42° Bé., with a content of 80 per cent of glucose. The concentrated sugar liquor is run onto large tables where it dries; when cold, it is cut into slabs, and these are clipped into smaller pieces for shipment. This is corn sugar, also called grape sugar. It may be crystallized by seeding it with glucose crystals, called dextrose in the trade. Sugar is slowly agitated during crystallization, which is slow; after 90 hours, the crystals are centrifuged, and are then 99.5 to 100 per cent pure. This is dextrose hydrate, perfectly white in color.

TABLE 51.—*Products from corn in 1939 (U. S.)**

		Value per Unit
Starch	1,120,264,541 pounds	2.62 cents
Sugar	467,153,433 "	2.92 "
Syrup	957,297,004 "	2.20 "
Oil	167,425,943 "	7.5 "
Oil cake and meal	32,570 tons	\$17.96

Source: Bureau of the Census.

The syrup from the first step is "corn syrup unmixed" used in candy making, in baking, and in preserving; with the addition of cane sugar, it becomes a table syrup, known for example as Karo.

Both corn syrup and corn sugar are of industrial importance, as indicated in Table 51.

OTHER PATENTS

1,998, production of sugar from dried sugar beet; 1,755,165, method of treating sugar beets to produce sugar; 1,750,756, manufacture of corn starch; 1,792,088, manufacture of soluble starch, by sodium hypochlorite; 2,216,753 and 4, washed sugars; 2,255,555, treating sugars.

PROBLEMS

During the harvest, 1000 gallons (sp. gr. 1.06) of cane juice is crystallized every day. The analysis is as given in the text. The recovery of sucrose is 65 per cent. How much sugar separated contains 95 per cent sucrose. How many pounds of raw sugar will be obtained per day? What size tubs would you select for holding the juice? Two tons of sugar beet containing 16 per cent sucrose are extracted. The recovery of sucrose is 60 per cent. How many pounds of beet sugar are obtained? In order to preserve the remaining sucrose, hydrated lime is added to the molasses, in an amount

sufficient to precipitate all the sugar as tricalcium saccharate $3\text{CaO} \cdot \text{C}_{12}\text{H}_{22}\text{O}_{11}$.
much lime will you need?

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1941, there were produced in the United States 140½ million barrels of oil, and from these, 25.882 million gallons of gasoline. These figures show that petroleum and its products are necessities in the modern world—necessities only to a certain degree for civilians, absolute necessities for a country's armed forces. It is to the chemical engineer, more precisely the oil engineer in every branch of the industry, that the nation looks for the vast amount of gasoline required, for improvements which will and do produce not only higher octane gas, and more efficient lubricants, but toluene explosives and butadiene for synthetic rubber.

Chapter 24

Petroleum and Its Products

When first obtained from the ground, before refining in any way, petroleum (rock-oil) is called "crude oil." It occasionally shows itself at the surface through seepage; it usually occurs at moderate depths; in some cases it may be sought by drill holes 5000 feet and more deep. When such a drill reaches an oil basin, the oil is frequently forced out under enormous pressures; gas, salty water, and sand usually accompany the oil. After a while which varies considerably, the flow becomes quieter; after some time it does not gush at all, and the oil must be pumped out; finally, no oil is obtained even by pumping; the well is dry. New wells are therefore constantly being sought. The oil prospector chooses lands possessing a geology which has characteristics indicating petroliferous strata; these characteristics vary in different fields, and in no case is it beyond doubt that a hole will reach oil. The scientific search for oil is supplemented by accidental discoveries, in the course of drilling for water, for example. If natural gas occurs, it is reasonable to prospect for oil;* it is by no means certain that oil will be found, but since petroleum consists of a mixture of hydrocarbons, the lighter ones such as methane, CH_4 , and ethane, may have escaped, leaving the main body of liquids and solids not far away. The heaviest hydrocarbons are solid; the intermediate ones

Discovery of Oil. It was not so much the genius of man which discovered oil; it was rather the oil which revealed its presence and forced upon his attention, by seepages which frequently coated small rivers, in Pennsylvania; by contaminating brines, much to the disgust of the (1806) salt refiners, as for the brothers Ruffner along the Kanawha in West Virginia; in the escaping gas, rich in vapors and known for centuries, as in the Baku peninsula, where the "eternal" fire gave a powerful support to religious cults (Zoroasters).¹ Only in more recent times, especially in the two decades past, has a more intensive search taken place, because the evident clues had been exhausted, and partly because petroleum has become a necessity to national as well as to civil life. To study of the soil for indications of petroliferous strata, which has already

¹ The Rodessa field, Caddo Parish, in Louisiana, was a gas field for many years; only in 1935 was it developed to carry oil.
² 478 and 474. in "Outstanding features of petroleum development in America," by David White, *Am. Assoc. Petroleum Geologists*, 19, 469-502 (1935).

been mentioned, there were added scientific methods: the revival of anticlinal theory, the measurement of temperature in adjacent wells in order to locate the anticlinal axis; gravitometry, including seismic or gravimeter apparatus; and the magnetometer.² Of these a few words might be said in description of the seismic method.

The seismic method for underground exploration is an adaptation of the study of low-lying, deeply buried rock formations, by the echo characteristics of time and direction of an artificial vibration, such as the explosion of a charge of dynamite; it is called the seismic reflection method. A portable seismometer is set firmly on hard ground; it consists of a post bearing a long pointer rigidly fastened to it, and a heavy weight suspended from the end of the arm. The post moves with the vibrations of the ground; the pointer magnifies them, and throws a point of light on the face of the weight which, in virtue of its inertia, does not respond to the vibrations. A moving-picture camera, set in rubber, records the path of the light; the rate of travel on the film gives the measure of time in thousandths of seconds. A charge of dynamite, let us say 11 pounds, at a depth of 95 feet is set off, and the first vibration as well as the subsequent reflections from the low-lying rock formation are recorded. The time for the reflection to travel upward to the surface and back to the depth; thus, in one case, two and 365/1000ths seconds indicated 185 feet. The slope of the strata is given by the shape of the curve. Many records are made in order to plot an area.³

More recent still are a geochemical method, the "halo method," and an electrical method, such as the Eltran. In the first method, soil surveys are conducted by measuring hydrocarbon content and mineralization in soil samples which are gathered with an ordinary auger. Eight analyses per square mile are preferred. The hydrocarbons are ethane, measured in parts per billion of soil, or the more concentrated liquid or waxy hydrocarbons. The significant high values, determined by statistical means, are plotted. If they form a pattern such as an aureole or halo, the area is positive and the petroleum deposit is roughly outlined by the pattern. Mineralization figures are also plotted, and give in a number of public land surveys a similar pattern for the same area.

Petroleum is found only in sedimentary rocks, and has its origin in the remains of plants and animals,⁴ which accumulated with clays and shales along the seashore. At a later geologic period, these strata were lifted and warped, forming arches (anticlines) and troughs (synclines), from one to several miles in width. Oil is found in the anticlines, having risen above the water; it may also be found in synclines, if the upper space (the

² *Ibid.*, 501.

³ In part from a radio broadcast by Dr. John P. Buwalda, California Institute of Technology, in a series on Recent Developments in the Geologic Sciences, under the name "Searchers of the Unseen," Jan. 4, 1936.

⁴ Geophysical Service, Inc., Dallas, Texas, publishes a bulletin called "Soil Surveys."

⁵ There have been many theories for the formation of petroleum deposits in the ground. The earlier ones was that of Engler who referred the formation of petroleum to a store of fatty acids of all kinds of life, but especially animal life; his opinion was based on laboratory experiments with menhaden oil, from which he produced a petroleum-like substance. C. Engler, *Ber. Deutscher Chem. Ges.*, 21, 1816 (1888). Among the present workers, Alfred Treibs assigns to plants the primary role in forming petroleum, to animal remains a secondary rôle. His statement is based on the spectroscopic study of the light absorption of petroleum, in which he thus identifies and estimates quantities of porphyrins of chlorophyll origin in a high percentage, while he also finds porphyrins of animal origin, but in much smaller amounts. *Ann.*, 510, 42 (1931). A brief summary of the older theories is to be found in "The examination of hydrocarbon oils and combustible waxes," D. Holden, Jr., by E. Mueller, New York, John Wiley and Sons, 1922.

bering antileak) is filled with the still lighter gas, also formed from deposits, and tapped as natural gas.

About 1850, several products were being manufactured from fatty coals (shale head or bituminous shale), one of which was an oil used for lighting and called "coal oil," which was taking the place of the disappearing whale oil distillate. It was for the purpose of securing raw material for this "coal oil" that Colonel Drake sank his now famous well at Titusville, Pa., in 1859; it was 69½ feet deep. Since then oil wells have multiplied; in the United States there were drilled, in 1936, 25,000 wells, of which 18,000 were productive. On December 31, 1939, there were 380,390 producing wells in the United States, and the average production over the year per well per acre was 9.2 barrels. In 1940, a total of 28,124 gas and oil wells were drilled, of which 19,125 are producing oil wells, 2282 are gas wells, and 6617 are dry.

When first tapped, the well may be a gusher, with many thousands of barrels per day; this output begins to decrease at once, and gradually tapers off until a pump is needed to bring up the oil. A life of 20 years is a rough estimate for a new pool.

A depth of 10,000 feet was reached in several oil wells in 1937, and was considered amazing, but wells are now being drilled deeper and deeper. In 1937 there were 29 wells over 13,000 feet, and of these, 22 are in California. Continental Oil Company reported one of its producing wells as having a depth of 15,004 feet.⁵ The cost of a 4000-foot well is close to \$50,000; a 10,000-foot well costs \$250,000 and more. Depth drilling has been helped by the development of rotary drilling; several new chemical agents and the application of acids have contributed.⁶

TABLE 52.—*Petroleum oil reserves of the world* as of January 1, 1939.*

United States	14,000	million barrels
Russia	5,000	" "
Iran	3,500	" "
Venezuela	2,500	" "
Iraq	2,500	" "
Dutch East Indies	1,600	" "
Rumania	700	" "
Mexico	600	" "
Columbia	400	" "
Argentina	200	" "
Peru	200	" "
Trinidad	150	" "
Others	550	" "
World total	31,900	million barrels
or	31.9	billion barrels

* "World Oil Reserves Put at 31 Billion Barrels," by V. R. Garfias and R. V. Whetsel, *Oil & Gas J.*, 37, Feb. 16, p. 32 (1939).

Petroleum Reserves. Taking petroleum from the ground means taking from a finite store, and at the rising rate of crude oil production, thought must be given to the extent of this store. For the world, by countries, the known reserves, that is, those established by drilling to the pool to establish a producing well, are as follows:

In some cases it is possible that an upper pool, which has been pumped out, is underlain by a new one. The Fox pool, Oklahoma, at the 2000-foot level, producing since 1936, was "on the pump" in October of that year; a new well, 8088 feet down, brought in a new producing pool, 6000 feet from the original one. It was gusher, with 8 to 10 thousand barrels a day. "The field that came in was the E. Savage, *The Lamp*, February, 1936.

"Science goes down an oil well," J. Arthur Sohn, *The Lamp*, December (1936)

lish its dimensions, are given in Table 52. For the United States, the relation between proven reserves and production over a period of years is shown in Figure 156. It would appear that the rate of discovery has more than kept pace with the rate of production. And yet the possibility of exhaustion after several decades exists. One means for conserving is to reduce and abolish waste, and that is being done by state regulations, by pro-rating the unit operation of pools.⁸ Another means is the more complete ex-

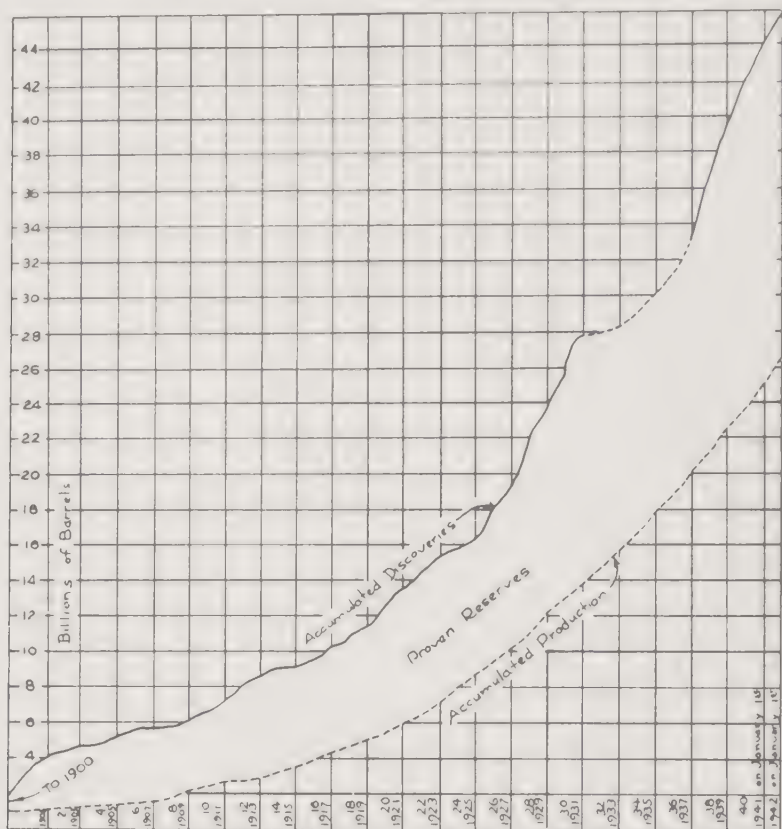


FIGURE 156.—A graph showing accumulated discoveries, proven reserves and accumulated production of crude petroleum in the United States. [Originally taken from the graph in *Bull. Am. Assoc. Petr. Geologists*, 20, 6 (1936); now extended by means of figures from the American Petroleum Institute.] The "accumulated discoveries" figures for 1938 and succeeding years were obtained by adding "net new reserves" to "accumulated production."

tion of the oil sands for their oil. It must be explained that the oil never always lies in sand, and that rarely is as much as 50 per cent of the total lifted to the ground; more often it is 30 per cent and less. To recover the residual portions of the oil, or at least much of it, flooding by water has given good results in Pennsylvania, but it must be added, poor results in Ohio.⁹ The ground formations must be favorable. Another means is maintenance of reservoir pressure by returning gas or feeding in air u-

⁸ A brief treatment of laws and regulations concerning crude oil production will be found in *Minerals Yearbook*, 674-5 (1936); *Minerals Yearbook*, 771-794 (1935). On conservation in general, read *Petroleum Shortage in the United States and methods for its alleviation*, L. C. Snider and B. T. F. *Bull. Am. Ass. Petroleum Geologists*, 20, 15 (1936).

⁹ See graph on p. 31, *Bull. Am. Assoc. Petro. Geologists*, 20 (1936).

are to the formation. The actual mining of the residual sands has been aged.

Oil fields in the United States are among the most important in the world. In many localities, oil derricks dot the landscape, for example, in Pittsburgh and Wheeling, W. Va.; in Los Angeles, there is an oil field within the greater city limits; farther north, in the Ventura field, some oil derricks are built over the sea. The relative importance of the oil producing states is best shown in Table 53. United States production in 1941 was 1,404,182,000 barrels (A. P. I.).

Table 53.—*Production of crude petroleum in the United States by states in 1940 (in barrels of 42 gallons).**

Texas	493,126,000	Michigan	19,764,000
California	223,881,000	Pennsylvania	17,353,000
Oklahoma	155,952,000	Montana	6,768,000
Illinois	146,788,000	Kentucky	5,193,000
Louisiana	103,961,000	New York	4,999,000
Kansas	66,270,000	Indiana	4,843,000
New Mexico	39,001,000	Mississippi	4,380,000
Wyoming	25,683,000	Colorado	1,350,000
Kansas	25,583,000		

Total United States 1,351,847,000

Average value at well \$1.00 per barrel

Minerals Yearbook (1940).

Oil fields in the world occur in Russia, in the Baku peninsula in the Caspian Sea, in Rumania, Galicia, Mexico, Venezuela, and the Dutch East Indies.

The production for the several countries is given in Table 54.

Table 54.—*World production of crude petroleum with major producing countries (1940) in thousands of barrels.**

United States	1,351,847	Trinidad	20,219
U. S. R.	212,909	Peru	13,427
Venezuela	184,761	Canada	8,955
Iran	78,592	Burma	7,979
Netherlands Indies....	60,830	Bahrein Island	7,074
Mexico	44,064	Sarawak and Brunei..	7,047
Rumania	43,231	Saudi Arabia	5,365
Ecuador	26,067	World total	2,149,378
China	25,725	1939 total	2,078,853
Argentina	20,486		

Minerals Yearbook, 1940.

The United States portion was 63 per cent, the Western Hemisphere's portion 78 per cent of the world total.

Transportation of Crude.* In the United States, much of the crude oil is processed in refineries situated near the wells, so that its transport is easy, namely, by pumping. Crude oil is, however, also sent great distances without having to be hauled by rail; if the freight bills had to be added to the cost of the oil, petroleum products would be much more expensive than they are. The crude oil travels through especially constructed pipelines laid in the ground along a purchased right of way, in sections 75

This edition goes to press the oil transportation situation is confused because of the partial loss of the tanker fleet by enemy submarine action. It is probable that more pipe lines will be built in the future. Meanwhile the railroads are transporting more oil than ever before.

TABLE 55.—Classification in 5 Classes of Petroleum Crudes, According to their "Base," from the Distillation-Analysis of 899 Samples of Crude from All Over the World [R. I. 379, U. S. Bureau of Mines, E. C. Lane and E. L. Garton (1951), condensed].

	A	B	C	D	E	F	G
	Paraffin base oil (weak-boiling)	Paraffin intermediate base oil (weak-boiling)	Intermediate Paraffin base oil (weak-boiling)	Intermediate base oil (weak-boiling)	Intermediate Naphthene base oil (weak-boiling)	Naphthene intermediate base oil (weak-boiling)	Naphthene base oil (weak-boiling)
A.P.I. gravity	49.7°	39.2°	29.5°	39.6°	15.3°	29.5°	24.0°
Specific gravity	.781	.829	.879	.827	.964	.879	.910
Four point	below 5° F.	below 5° F.	40° F.	below 5° F.	40° F.	below 5° F.	below 5° F.
Per cent sulfur	0.1	0.25	0.32	0.33	0.81	0.36	0.14
Saybolt Universal viscosity 100° F.	34 seconds	41	120	29	4000	47	55
Cloud	green	greenish-black	greenish-black	green	greenish-black	greenish-black	greenish-black
Distillation 1st drop	93° F. (34° C.)	91° F. (33° C.)	176° F. (80° C.)	81° F. (28° C.)	280° F. (138° C.)	148° F. (59° C.)	315° F. (157° C.)
1st oil test							
Gasoline and naphtha	45.2%	32.0	5.8	38.6	2.9	21.3	1.1
Kerosene	17.7%	17.2	nil	4.9	4.5	nil	nil
Gas oil	8.3%	10.6	27.8	17.3	10.6	34.6	55.5
Naphthene lubricating	9.8%	10.9	20.4	10.9	8.6	10.4	14.2
Medium lubricating	3.4%	5.2	nil	6.3	6.7	7.0	4.7
Viscous lubricating	nil	nil	nil	nil	1.020	4.7	11.6
Residue	14.7%	23.5	36.4	22.1	58.4	21.4	12.7
Distillation loss	.9%	.6	.4	1.4	1.9	0.6	0.2
Carbon residue of residuum	1.1%	6.2	6.9	7.3	18.2	8.7	4.5
Carbon residue of crude	0.2%	1.5	2.5	1.6	10.6	1.9	0.6
Key fraction No. 1. (250-275° C.) 482-527° F., 750 mm. pressure.							
Per cent cut	6.8%	6.5	7.1	5.8	5.1	10.1	19.6
A.P.I. of cut	44.7°	40.6	36.4	37.0	37.0	30.2	27.9
Key fraction No. 2. (275-300° C.) 527-579° F., 40 mm. pressure.							
Per cent cut	4.4	5.7	9.0	4.9	8.2	6.0	7.3
A. P. I. of cut	34.4°	29.3	30.0	24.9	19.5	24.0	16.5
Viscosity at 100° F.	110 seconds	120	120	165	240	230	over 400
Cloud test, in °F.	90	90	90	80	70	90	below 5

If the fraction No. 1 needs 40.0 A.P.I. or lighter, the lower boiling fraction of the oil are paraffinic; if it needs 33.0 A.P.I. or heavier, they are naphthene; if the gravity lies between 33.0 and 40.0 A.P.I., they are intermediate.

If the gravity of key fraction No. 2 is 30.0 A.P.I. or lighter, the lower-boiling fractions of the oil are paraffinic; if it is 27.9 A.P.I. or heavier, the fraction is naphthene; while if the gravity lies between 20° and 30° A.P.I., the fraction is intermediate.

long or more. The right of way is patrolled for leaks and each section has storage tanks and a pumping station. For Buffalo, the preceding station is Clean, N. Y., where the oil enters an 8-inch line under a pressure of 100 pounds. The capacity is 25,000 barrels a day (1942). When a ridge is crossed the line is so constructed that one leg is downhill so that by siphon effect it will help pull the oil up the hill. In this way crude oil from Oklahoma reaches Bayonne, N. J., and Marcus Hook, Pa., while Texas oil can be sent to Chicago (Whiting, Ind.) or Buffalo, N. Y. No pipe line crosses the Rocky Mountains.¹¹ A 12-inch pipe line 237 miles long running from South Portland, Me., to Montreal, operated by eight pumping stations, has a capacity of 60,000 barrels daily for light crude oil, or 40,000 barrels for light oil; it was completed in 1941. Of the total crude oil reaching the refineries, 320.3 million barrels were transported by boat, 939.9 by rail, and 40.4 by rail and truck.

Formerly oil was burned as such for its fuel value, and to a small extent is still done; but, by far the greater amount is refined, and only that which cannot be made to yield any of the more valuable products is burned under boilers (fuel oil, bunker oil). On distilling crude oil, there are obtained: gases, which are usually burned under boilers; gasoline, for use in internal combustion motors with spark firing; solvent naphtha; kerosene, for use as fuel oil, lubricating oil, paraffin wax (hard wax), petrolatum (soft road tar, coke, and other products. A selected part of the fuel oil is used as Diesel oil.

Classification of Crudes. An eminently satisfactory classification of crudes has been developed by the U. S. Bureau of Mines; the main features are given in Table 55. Class A comprises the paraffin-base crudes, which are paraffinic; these contain mainly paraffinic hydrocarbons in all their fractions; their residue in the still becomes the much-sought after "cylinder stock." Straight-distilled gasolines from this crude would be paraffinic, and have "good knocking" properties. Naphthene base oil, class G, contains mainly naphthenes, that is, cyclic compounds which are saturated, with side chains which are naphthenic and paraffinic. Naphthene base and intermediate naphthene base, class E, may contain much black, brittle, almost infusible material, although they often do not; when they do, they fit the description of asphalt-base oils. Naphthenes are hydrocarbons of the benzene series, rich in hydrogen, with ring formation; they carry side chains (given below) which may be naphthenic or paraffinic. The paraffins

Origin of samples in Table 55:

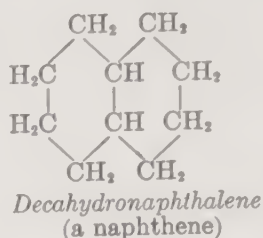
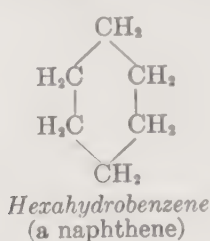
Virginia, Ritchie Co., Lost Run field	E. Wyoming, Park Co., North Sunshine field
Wyoming, Lincoln Co., Chandler field	F. Texas, Austin Co., Raccoon Bend field
Alabama, Webster Parish, Cotton Valley field	G. Texas, Refugio Co. Refugio field
Alabama, Seminole Co., Seminole field	

These samples are typical of the class it represents. The seven classes listed in the table are:

A. Paraffin base: distillates paraffinic throughout	E. Intermediate-naphthene base: light fractions intermediate, heavy fractions naphthenic
B. Intermediate base: light fractions paraffinic, heavy fractions intermediate	F. Naphthene-intermediate base: light fractions naphthenic; heavy fractions intermediate
C. Intermediate-paraffin base: light fractions intermediate, heavy fractions paraffinic	G. Naphthene base, distillates naphthenic throughout
D. Intermediate base: distillates intermediate throughout	

A map of the oil pipe lines may be obtained from the *Oil and Gas Journal*, Tulsa, Okla., for a price. The same map on its other side shows the trunk natural gas lines.

are the straight-chain, or branched-chain hydrocarbons; iso-octane, heptane, cetane, presented farther on,



are examples. The naphthenes merge into oils rich in aromatics, the derivatives of benzene and higher members of the series C_nH_n , again an endless assortment of side chains.

The crudes differ also in the relative amounts of lower- and higher-boiling constituents: some are so thick that they barely pour; others as fluid as kerosene. This is well brought out in Table 55; in fact, one of the purposes in giving it is to answer precisely the question: how much gas does crude oil contain? The amount varies, but definite figures are presented. An overall yield will be found elsewhere in the chapter.

The greatest demand is for gasoline, and in order to increase the supply of this material, the higher-boiling hydrocarbons are heated to an excessive temperature which causes them to decompose into more volatile, lower-boiling hydrocarbons, such as in gasoline; the operation is called "cracking," namely, into smaller molecular fragments.

Exact boiling points and densities cannot be given, but the following may serve as guides:

Gasoline has a density of 55-60° Bé., and boils at 100-400° F.* (37-8-204° C.).

Kerosene has a density of 40-45° Bé., and boils at 400-600° F. (204-315° C.).

Fuel oil varies greatly; it is sometimes 36-40° Bé.

Lubricating oils have a density of 28° Bé. for the lightest engine oil, to very high densities.

REFINERY OPERATIONS

The older refining units were crude oil stills which separate the material into a crude gasoline fraction, a crude kerosene, an intermediate fraction, and a paraffin oil fraction; coke is left in the still, to be knocked out by hand. The operation was discontinuous, and cracking was done in separate stills. The preferred method today is the continuous pipe still with fractionating tower. The new method makes full use of the fractionating tower for the separation of the various fractions, which are taken at various levels. A few general considerations regarding such "bubble towers," as they are called in the oil trade, are in order.

The Bubble Tower. In a normal column, only one well-fractionated product can be made; it comes off overhead. The number of plates fixes the quality of the overhead product. Refluxing, that is returning to the column a portion of the condensed distillate, has the effect of reducing the number of plates necessary for a given separation; the greater the reflux ratio, the smaller the number of plates required. The place to put back reflux is

* Bé. scale here is the scale for "lighter than water," see appendix.

composition of the liquid on the plate is the same as that of the refluxed liquid. When a number of cuts are drawn, their fractionation is not complete and must be supplemented by a small column called the stripper, or each cut, in which the cut is freed from all more volatile constituents than its set standard. The "deck space" (distance between plates) must be sufficient to allow the vapor to disengage itself from the liquid; it varies from 10 to 24 inches. The number of plates varies from 5 to 25, averages 11 to 15 instills for one overhead cut. The vapor velocity is at maximum; it is too high if it forces the liquor off the plates; 2 feet per second is average, 3.5 is high. A bubble tower handling 5500 barrels of crude per day, in one instance, is 92 feet high, and 6 feet in diameter; it is well lagged to preserve the heat.

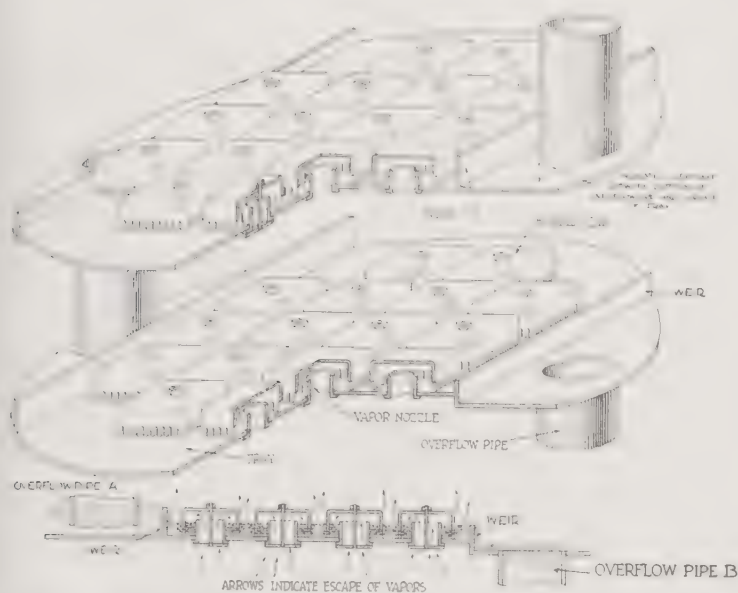


FIGURE 157.—Two plates in a bubble tower, showing the domes or bubble caps, the overflow or rundown pipes, and the weirs. (From the Pennsylvania Grade Crude Oil Association, Oil City.)

Each plate has a number of small chimneys for the rising vapors, covered with bells or caps so that the vapor must bubble through the liquid on the plate. A downcomer carries the liquid to the next lower plate, and is surrounded by its liquid. Baffles are placed across the deck so that the liquid takes a long path before it reaches the next downcomer. The capacity of a bubble tower depends upon its diameter and height, its efficiency upon the number of plates, the construction of caps, deck space, reflux procedure, and the velocity of vapors.

A tower unit would be called efficient if the gasoline fraction had an initial boiling point of 400°F . and the kerosene an initial boiling temperature of 450°F . An overlap of 25°F . would not be bad; an overlap of 50°F . would be poor efficiency.

Oil columns are operated at atmospheric pressure, at higher pressure and with vacuum; the oil is distilled dry, or with a supply of steam to it. When higher pressures are used, the temperature must be higher. The temperature at the base of the still must be such that the material is boiled.

Continuous Distillation-Skimming Unit. The method of working is illustrated by the diagrammatic flow sheet in Figure 158 of a 7000-per day unit of the Producers and Refiners Corporation¹³ at Tulsa, Oklahoma. The crude oil picks up heat in the gasoline vapor heat exchanger, then, after passing through a settler for removal of any water, more heat in the crude-oil heat exchangers. At a temperature of 350° F., it now enters the tubes of the furnace, where six oil burners raise its temperature to 700° F., but below cracking temperature, for this is a skimming unit, not a cracking unit.

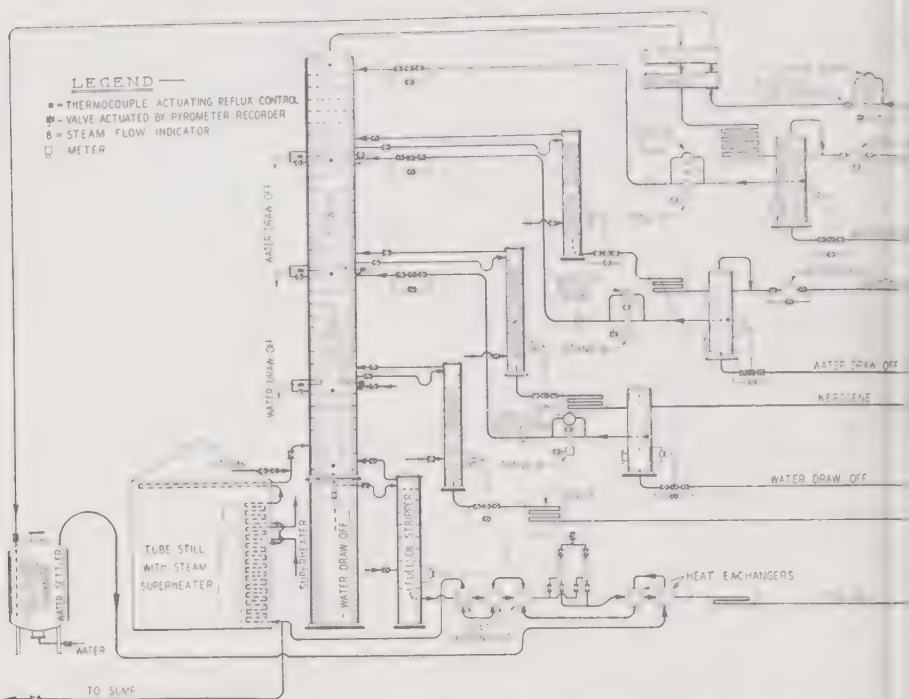


FIGURE 158.—Diagrammatic flow sheet for a 7000 barrel Tulsa unit, showing still, bubble tower, four auxiliary plate towers used as strippers, with densers, after coolers, three reflux pumps, and heat exchangers. (Courtesy National Petroleum News.)

a plant for the separation of the gasoline and other fractions just as they are in the crude. The mixture of hot oil and vapors enters the bubble tower and fractionation takes place. The tower is 10 feet in diameter, and 40 feet high. Gasoline vapors are taken off overhead, that is, at the top of the tower; a naphtha cut just below the top; next a kerosene cut; then an oil cut; while finally the residual oil forms the fuel oil cut at the bottom of the still. In conformance with the statements on fractionation, for some cuts refluxing is necessary, and there are returned to the still a part of the gasoline, now cold, a part of the naphtha, and a part of the kerosene.

¹³ "One man operates new 7000 barrel pipe still skimming unit," Allen S. James, *Nat'l. Petroleum News*, 21, 73, Nov. 27 (1929).

old. The effect of the return of such cooled liquid to the point in the where material of similar composition is met by it, is essentially to the vaporization of the more volatile of the constituents. Each fraction is cleared of any admixed higher fraction in a small auxiliary plate, which receives superheated steam. (See Fig. 158.) For the kerosene, for example, the stripper returns overhead to the still a mixture of kerosene, naphtha and water vapors. Condensed water in the bubble tower is sent out at the points indicated.

The fuel consumption, exclusive of the steam, is 1.5 per cent of the output. This unit replaces a battery of seven shell stills of the older type.

The chemical refining of the several products was done formerly by treatment with 66° Bé. sulfuric acid (generally 3 pounds of acid to each barrel of oil), followed by a water wash, then a dilute caustic soda wash. The amounts of sulfuric acid consumed are so great that methods for recovering it were developed; a plant for recovering the sulfuric acid from



FIGURE 159.—View of the tube still, in the 7000 barrel unit at Tulsa. The bubble tower can just be seen in the rear of the picture.

"Sulfuric acid" is part of many refineries. For sulfur-containing crudes the chemical treatment of the fractions includes agitation with caustic soda treated with litharge (PbO). Certain crudes require a special treatment with metallic oxides such as the one devised by Herman Frasch.¹⁴ There are now other methods for purification, for the purpose is no longer to remove all the unsaturated hydrocarbons, but only part of them. A valuable constituent may be recovered from the purification treatment to make the source of a valuable resin (Chapter 35). A modern method of purification which saves the by-products without injuring them is the Solvay process, which employs liquid sulfur dioxide. For this treatment, sulfur dioxide is introduced near the top of a tower completely filled with the liquids; the well-cooled distillate (gasoline, naphtha, kerosene, or other fraction) is introduced near the bottom, both in spray form. The vapors of the distillate must rise through the body of the liquid sulfur dioxide; the droplets of the fresh solvent must sink through the layer of hydrocarbons. Two layers continue to form, the sulfur dioxide being the lower one (sp. gr. 1.45 at 68° F.); the hydrocarbons form the upper one. The continual removal of the liquids to make room for the incoming distillate. The asphaltenes, carbogens and sulfur-containing impurities dis-

solve in the sulfur dioxide, and flow out with it. In a separate vessel the sulfur dioxide is vaporized, re-compressed and re-cycled; there is behind the extract, which may have a commercial value. The upper part dissolves a small amount of sulfur dioxide; in a separate still, this is driven off by a gentle heat, and saved; the refined product is left.

Cylinder Stock and Wax Distillate. Many crudes give distillates in the following order: light naphtha, heavy naphtha, water-white, gas oil, oil, then wax distillate, which Figure 156 does not show, but is indicated in Figure 158, and the residuum, in certain cases the most valuable product. The Pennsylvania grade crudes, which are always class A, leave a residuum so low in suspended carbon and so free from asphaltic impurities that it forms an article of commerce under the name of "cylinder stock."¹⁵ This is refined in a vacuum column still with steam injection, giving a "press wax distillate" overhead, and "600 steam refined" [that is, heated to 315.5° C.] as a bottom product, not volatilized; this latter is diluted with naphtha, filtered, chilled, and its suspended soft wax separated by centrifuge, giving petrolatum. The clear solution is passed through a filter to drive off the naphtha; it may be bleached by passing it through granular clay, and there results "bright stock" with viscosity, for example, of 180 seconds at 210° F.

The wax distillate carries the hard wax. It is chilled to 26° F. (– 1° C.), and the suspension forced under a pressure of 300 pounds into a press set in a room which is kept cold. The press may be, for example, 36 feet long, with 350 circular cast iron plates, 5 feet in diameter. A filter cloth is cotton duck; the press has central feed. Once a day the press is opened and the wax removed; as it still contains 40 per cent oil, it is "sweated," that is, warmed in shallow pans with false bottom on which the wax rests, while the oil flows into collecting troughs. The wax left in the pans, now free from oil, is melted and run through bone char in cylinders 2 feet wide and 20 feet high, to remove the color. The white wax is pressed into blocks for shipment, or is made into candles. In addition, it is used in laundries, for waxed papers and drinking cups, and for a variety of household purposes.^{15a}

The oil filtrate from the wax press passes to a still, with steam injection, to give a gas oil, a non-viscous neutral oil, and as residue, a viscous neutral oil. The latter is filtered through granular clay, and becomes a finished viscous neutral, with viscosity of 180 at 100° F.

Lubricating oils for the market are then produced by blending viscous neutral and bright stock in various proportions.

The value of cylinder stock is reflected in the price per barrel of Pennsylvania Grade crude, which was \$2.32 (Bradford) and 1.97 (Spartan, Pa.), while Oklahoma was 1.02, Panhandle 0.81, West Texas 0.75, and

¹⁵ Example of cylinder stock:

Penn stock, viscosity	100-125 sec. at 210° F.
	1600 sec. at 100° F.
Constat stock, viscosity	125-130 sec. at 210° F.
	3060 sec. at 100° F.

In early 1937, the quotations for cylinder stock in tank car lots ranged from 14½ to 18½ cents per gallon.

^{15a} An interesting 29-page pamphlet on "Candle manufacture, with special reference to tapers," by Professor N. N. Godbole, has recently been published; it depicts the teaching of the art of candles in India, and the materials available, with their properties and costs. Benares Hindu University, Benares, India, 1935.

ge. \$1.00. The higher value is one reason also that it is worth while in Pennsylvania to flood the oil sand with water to recover the residual

THE DUBBS CRACKING PROCESS

Several proposals have been made for a system which would allow the simultaneous distilling of the crude and the cracking of its heavier hydrocarbons, in an apparatus which would permit a continuous, or relatively continuous, operation. In the Dubbs process (Fig. 160), the preheated oil (750°F. or 399°C.) is circulated through 4-inch steel tubes heated directly in a furnace to 840°F. (449°C.) under a pressure of 350 pounds. Leaving the heating coil the superheated oil enters a vaporizing chamber

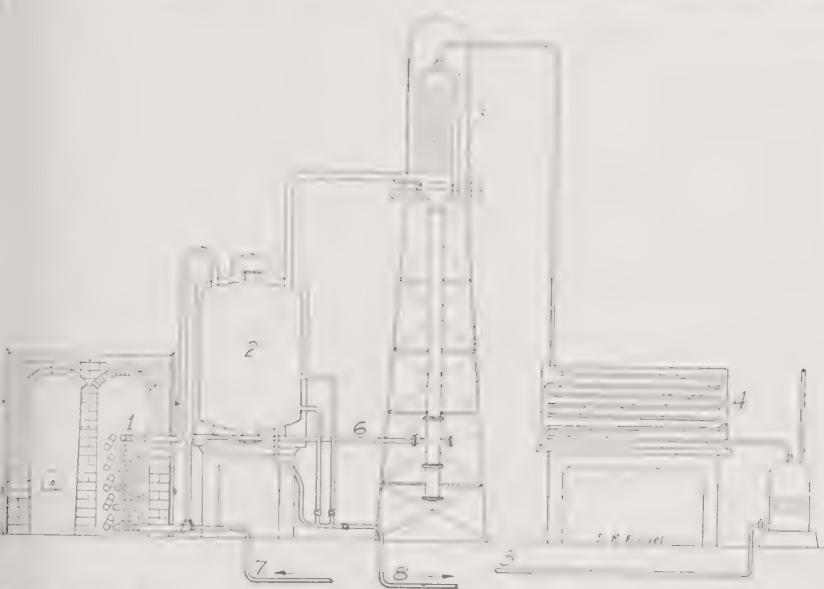


FIGURE 160.—Scheme for simultaneous distilling and cracking of crude oil (Dubbs patents). 1, heating coils; 2, vaporizing chamber; 3, dephlegmator, cooling coil not shown; 4, condenser for gasoline; 5, line from receiver to storage tank; 6, high-boiling parts of vapors condensed and returning to heating coils, joining fresh crude oil from 7. The operation is continuous. The use of 3 for topping crudes is given in the text.

it separates into gases and vapors which pass through a dephlegmator condenser; a liquid consisting of heavy portions which form the residuum and a solid, coke, which accumulates in the bottom of the chamber. The dephlegmator reduces the temperature of the vapors so that only the light fraction passes it; heavier hydrocarbons are condensed and drop down the reflux leg from which they are returned with fresh oil to the heating coils. The dephlegmator has a cooling coil in which the fresh oil circulates; by varying the quantity of cold oil sent in, the temperature is controlled; by passing this coil that the fresh oil is preheated. The action in the dephlegmator is controlled further by spraying oil directly into the vapors; fresh oil is added, and its temperature is raised sufficiently so that such gasoline as remains is vaporized and passes to the condenser with the uncondensed

vapors from the chamber. Such fresh oil which is made to give up gasoline is called "topped oil"; the remainder of such oil also drops in reflux leg and from there is pumped through the heating coils.

The functioning of the system is controlled by the pressure under which it operates, and this is determined by the position of a needle valve release valve, set at the receiver for the condensed vapors which leave cold-water condenser. The liquid in the distillate receiver is treated chemically if necessary, to produce the purified gasoline.

The Dubbs process¹⁶ provides admirably for the handling of such crudes as contain no lubricating oil fraction; for they are made to yield increased amount of gasoline; the other products are fuel oil, obtained from the residuum by merely cooling it, and coke. The operation is limited to continuity by the capacity of the vaporizing chamber for coke, and amount of coke deposited will vary with the kind of crude used; by building two chambers, this limitation is removed. There remains in that case fouling of the heating tubes by the coke which accumulates there; a period of 11 days is considered fairly good. In order to lengthen this period, the system must be fed not with crude oil, but with a fraction obtained in the course of a previous distillation in a bubble tower. This procedure has become the general practice, and the fraction is called cracking stock. In general, for every barrel of gasoline, there is formed a barrel of "heavy residue" (see under bunker oil).

Other important processes¹⁷ which crack by heat and pressure are the Cross, the Holmes-Manley, and the Ellis. In the Cross process, as in the Dubbs, the oil is passed through a coil laid in a furnace, and then delivered into a horizontal vaporizing chamber which receives no outside heat; operating pressure is higher than in the Dubbs, namely 600 pounds. The Cross process has been very successful. In the Holmes-Manley, the oil is heated in stills 3 feet in diameter and 40-feet high, provided with stirrer at a pressure of 175 pounds. The Ellis is a tube and tank system.¹⁸

As a rule, when crude oil is fed directly into the tube stills of a cracking unit, the latter are fouled by coke; the vaporizing chamber also collects coke. In the *De Florez process*,¹⁹ a way has been found to handle crudes so that there will be no coke formation. The apparatus consists of the heat exchanger, bubble tower, reflux cooler, pumps, and a circular, vertical still. In the standard set, the pipes are 42 feet tall, of special steel, number 102. They are set in two concentric circles, and so spaced that the rear ones receive radiations as fully as the front ones.

The pressure at which the bubble tower is operated is the factor governing the nature of the products. With the pressure in the tower 80 pounds, the still just before entering the furnace 330 pounds, and the temperature at that same point 1000° to 1100° F. (531° to 590° C.), a Venezuelan

¹⁶ *Chem. Met. Eng.*, 31, 1006 (1924) and U. S. Patents 1,123,502, 1,231,509, 1,195,506, 1,219,506.

¹⁷ Descriptions and sketches will be found in *Chem. Met. Eng.*, 31, 812, 849 (1924).

¹⁸ There are 33 different processes for cracking, 57 installations are the plant's "Own," 520,000 barrel capacity per day; 55 are Dubbs with 387,100 barrels; 22 are tube and tank with 32,000 barrels; 41 are Cross, with 200,600 barrels; 19 Holmes-Manley, with 186,500 barrels; 9 De Florez with 32,000 barrels; 10 Donely with 35,000 barrels capacity per day. There were 8 combination units skimming the crude and at the same time crack the heavier molecules, with a crude oil capacity of 95,000 barrels a day. From "Petroleum refineries including cracking plants in the United States on Jan. 15," R. G. Hopkins and E. W. Cochrane, *U. S. Bureau of Mines, I. C. 6906*.

¹⁹ "Control of gasoline and fuel oil quality in cokeless cracking process," Paul Truesdell, *Natural Gas and Petroleum News*, 21, 69, part 2, May 1 (1929).

(to 8 per cent gasoline) gave as products: 30 per cent gasoline, 63 per cent fuel oil, and 7 per cent fixed gases. The gasoline produced boiled between 100° and 384° F. (38° to 196° C.).

With lower pressure, for example 20 pounds, the gasoline yield is smaller, and fuel oil fraction greater. Increasing the temperature and pressure on the still tower raises the antiknock value of the gasoline, but at the same time raises also the absolute quantity of fixed gas.

With a pressure of 100 pounds in the furnace the De Florez is a vapor-phase cracking unit; with 400 pounds it is a liquid-phase cracking system.

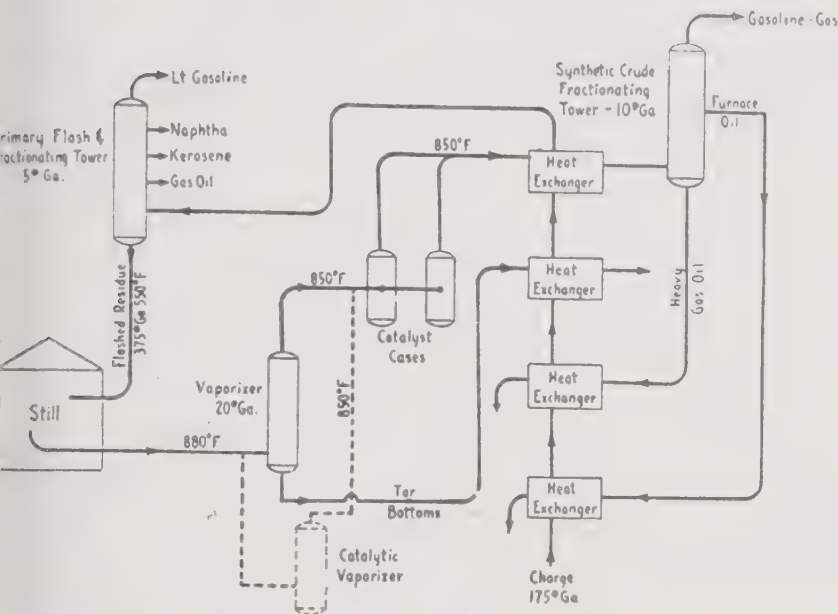


FIGURE 161.—General flow diagram of the Houdry catalytic cracking process, showing crude-topping combined with catalytic cracking. (From "Catalytic processing by the Houdry process," *Oil and Gas Journal*.)

The Houdry Process: The best known catalytic cracking process is the Houdry process, in which the cracking is performed while the oil is in contact with a solid catalyst consisting of activated hydrosilicate of alumina in molded pellets. The charge passes from a tube still to a vaporizer and thence to catalyst cases, which they leave to reach a heat exchanger, which in turn leads to a fractionating column. Gas, gasoline, furnace oil and heavy oil are produced from a crude oil, as well as tar bottoms from the vaporizer. The catalyst must be regenerated after a time, and this is done in a separate case, without removing it. By installing two cases, the operation is continuous, for one case functions while the other is being regenerated. Heat exchangers transfer the heat of the outgoing hot oil to the incoming charge. In the figure adjoined, a primary flash tower functions on the same principle. The temperature in the catalyst cases is 850° F. (455° C.).

"Catalytic processing by the Houdry process," by Eugene Houdry, Wilber F. Burt, A. E. Pew, W. A. Peters, Jr., *Oil and Gas Journal*, 37, 40-48 (1938).

The advantages of the Houdry process are: the production of high-grade gasoline of aviation grade with high yield (45%) in one pass; low production; no production of heavy fuel oils; and flexibility in meeting seasonal variations in demand of furnace oil, fuel oil, gasoline. The process reduces the content of sulfur, which the crudes or charged fractions contain, to below 0.1%.

Fluid Catalyst: A catalytic cracking process usually has one handicap, namely, that every so often the catalyst must be taken out of operation, the catalyst chamber purged, and the accumulated carbon removed by combustion with oxygen. (See also under Hydroforming, p. 443). In the fluid catalyst* process the cracking operation is continuous, because the catalytic mass is so chosen that under the operating conditions, it flows like a liquid, and may be moved slowly out of the zone of catalysis.

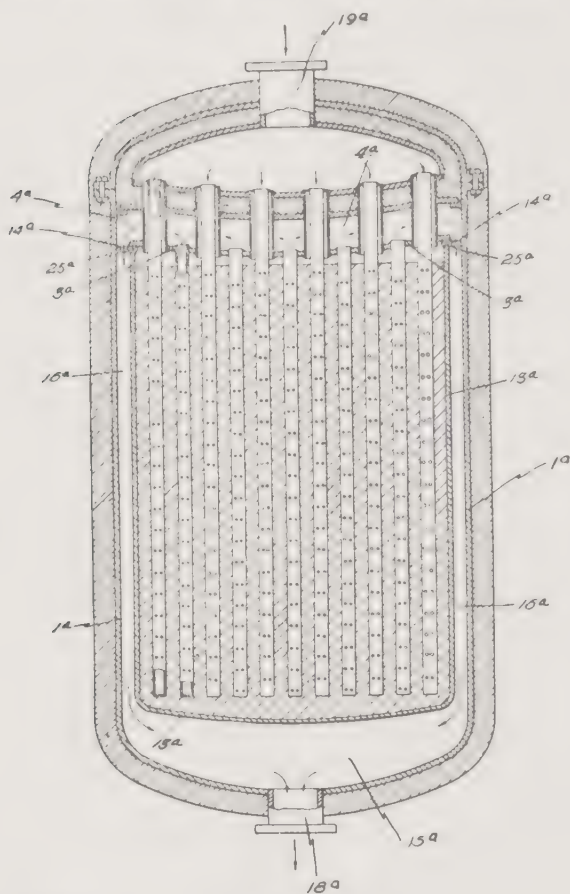


FIGURE 162.—Catalyst chamber of the Houdry catalytic cracking installation. Fluids enter the contact mass through openings in the tubes extending downward into the mass. They leave through similar tubes somewhat shorter. The reaction products pass down next to the outer shell; a more uniform temperature results. (From "Catalytic processing by the Houdry process," *Oil and Gas Journal*.)

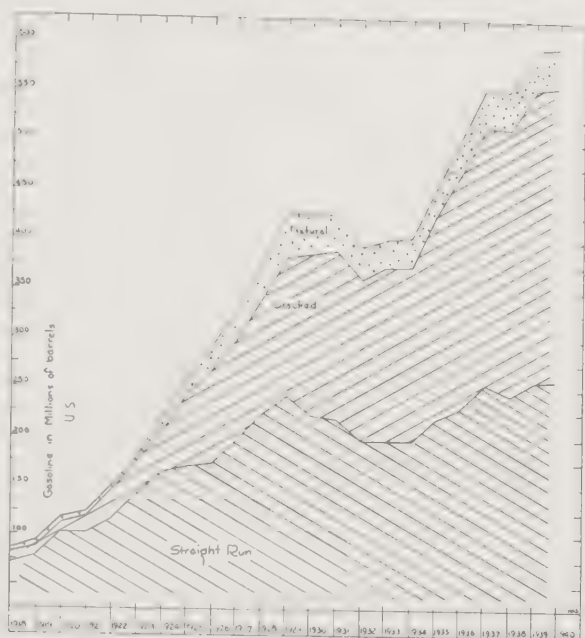
revivification zone, whence it is returned to the catalyzing zone. The plants embodying this principle were constructed in 1941, each producing about 6000 barrels of gasoline a day.

For the purification of gasoline cracked by any method the standard sulfuric acid process is used, or the Edeleanu liquid sulfur dioxide process already mentioned; other special processes such as the Halloran, in which the gasoline is treated with much acid in 3 steps, at low temperatures

* "Revolution in refining," *The Lamp*, 23, 12 (1941).

-178° C.), and the Lachman process, in which the hot hydrocarbon meets a concentrated zinc chloride solution,²⁰ have met with success. In the purification, it is customary to stabilize the cracked gasoline feed, which means in this case driving out its dissolved propane and other gases by heat.

FIGURE 163.—Curves showing the yearly amounts of straight, cracked, and natural gasoline, which, with benzene (not included), make up the motor fuel figure in the United States, based on graph in *Oil and Gas Journal* (May 21, 1935), extended.



In the McAfee process, 5 to 8 per cent anhydrous aluminum chloride is added with an absolutely dry oil fraction, at atmospheric pressure, with shaking. The temperature is 550° F. (288° C.), and the period 48 hours. An excellent quality of gasoline is obtained, which requires only a wash with alkali. The success of the process depends upon a cheap enough source of aluminum chloride. For this purpose a remarkable process has been developed, in which a mixture of bauxite and carbon is projected by a chlorine containing oxygen and nitrogen into a chamber held at the same temperature. The chloride forms granules which drop out of the way of incoming materials.²¹

The average gasoline yield by cracking is at best 60 per cent on the original stock; by combining hydrogenation with pressure cracking, the yield may be increased to 108 per cent. The reduction of available crude favors large scale adoption of this combination process.²²

The relative importance of straight-run gasoline, cracked gasoline and other motor fuels is shown in Table 56:

Natural gasoline is the liquid which accompanies the "wet" natural gas in many regions; it is removed by passing the gas through a large number of oil towers. After the oil is saturated, it is heated gently, the gas is collected, and the oil, after cooling, is used over again. Activated car-

Chem. Met. Eng., 42, 414 (1935).

"Deep aluminum chloride," A. M. McAfee, *Chem. Met. Eng.*, 36, 422 (1929), or U. S. Patent

Am. Ass. Petr. Geol., 20, 43 (1936).

TABLE 56.—United States production of motor fuel in 1940.
(Barrels of 42 gallons).*

	Barrels	% of the crude oil
Straight-run gasoline	263,584,000	20.4
Cracked gasoline	294,365,000	22.7
Natural gasoline (of which about 36 mil lion barrels were blended at the refinery)	55,249,000	
Benzol	3,161,000	
Total	616,359,000	

* Minerals Yearbook, 1940.

bon, silica gel, and activated alumina, as well as other adsorbing agents, also in successful use, replacing the straw oil.²³

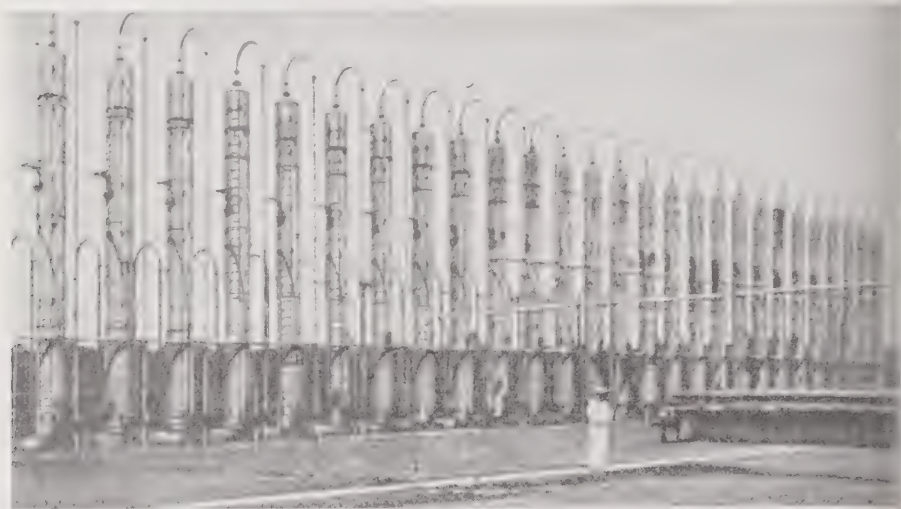


FIGURE 164.—A natural gasoline extraction plant; the wet gas passes through the 27 towers in succession, entering at number 1, leaving at number 27. The fresh oil enters at 27, and travels toward 1. Monroe field, Louisiana. (From the National Geographic Magazine.)

Petroleum Coke, Bunker Oil. In the old batch operation with stills, an accumulation of coke took place gradually, so that every seven days, the still had to be cleaned out by removing with picks and bars the coke which had formed. The smaller amount of coke which is formed in the pipe still is not allowed to deposit anywhere, but is swept along with the crude through the still, carried into the bubble tower, and discharged with the residuum, which may also carry asphaltic matter. Much of this residuum forms the fuel in the refinery. Some of it is sold for fuel for steam boilers, at perhaps 3 cents a gallon under the name bunker oil.²⁴

The demand for coke in the meantime has become insistent; to meet some of the residuum is run into a batch still which has been retained for the purpose, and distilled to dryness. A certain amount of fuel oil is

²³ "Recovery of vapors," C. S. Robinson, New York, Reinhold Publishing Corp., 1942.

²⁴ Two samples of bunker oil

	Sample 1	Sample 2
A.P.I. gravity	15.9	19.9
Saybolt viscosity at 100° F.	207	155
Flash (open cup)	225° F.	200° F.
A.S.T.M. Pour (max. for 115° F.)	50	45
A.S.T.M. Pour (min. for 220° F.)	-10	-20

1, and the coke is allowed to deposit. It is later removed as in the old process and sold for 6 to 7 cents a pound for making electrodes. Petroleum is ash-free.

Another source of bunker oil is the heavy residue from the cracking process, with perhaps a small addition of gas oil to make it more fluid. The process to "stabilize" bunker oil, so that it will not develop sediments on contact and in storage, is the Goodwin process, which consists of "chemical and mechanical treatment of the residuum leading to two materials of value: a stabilized fuel oil, merchantable as Bunker A, B, and C, and a high-value residuum suitable as a refinery fuel or a briquette binder."²⁵

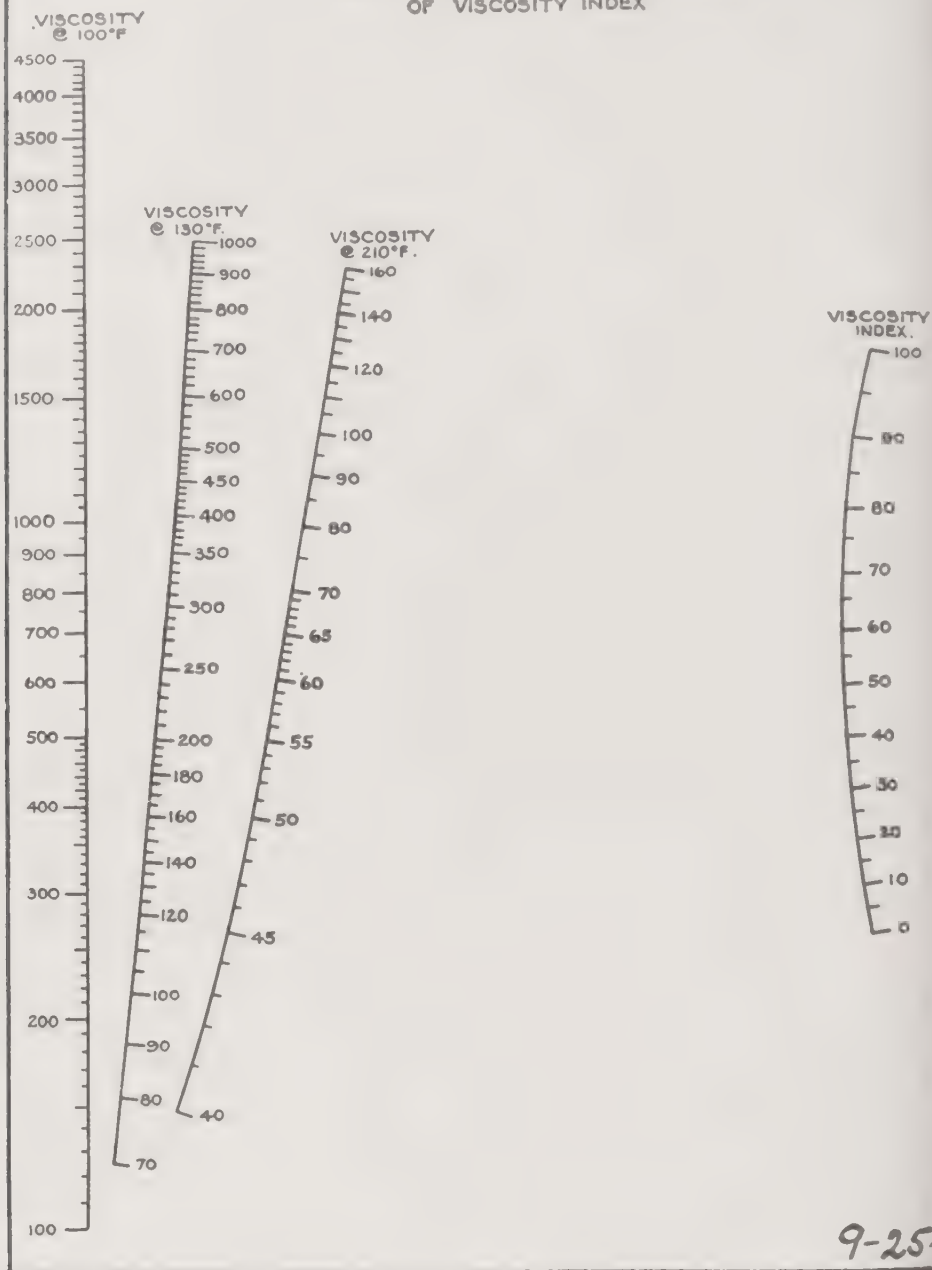
HYDROFINING AND THE PURIFICATION OF LUBES

Hydrofining. Hydrofining is the high-pressure catalytic hydrogenation of low-grade petroleum fractions, to produce high-grade standard products, and of low-grade products with superior qualities. The process permits the production of a lubricating oil possessing all the desirable properties of such an oil, a result never before attained. Another adaptation is the conversion of low-grade crudes and refinery residues into gasoline low in sulfur, without the use of coke. Still another is the transformation of poor quality gas oil into hydrogenated gasolines with high antiknock properties. The present cracking methods allow the upgrading of a part of the stock charged; the remainder is degraded into tars and coke. With hydrogenation, however, it is feasible to upgrade all the stock charged, and transform it into more valuable, lower-boiling distillates.

The lubricating fraction to be treated, either paraffin base, naphthenic or mixed, is pumped under a pressure of 3500 pounds per square inch. Hydrogen gas under the same pressure, through a heat exchanger, then through gas-fired heating coils, at a temperature of 800° F. (427° C.) to four reaction chambers, which contain the sulfur-resistant catalyst. The reaction chambers are 40 feet high, 3-inch internal diameter, forged from nickel with wall 7 inches thick. The catalyst is molybdenum oxide deposited on alumina shaped into 1-inch cubes. In these chambers the molecule is rearranged into its most stable form (stabilization), combined with hydrogen, while at the same time the elements oxygen, nitrogen, and sulfur form their relative hydrides, leaving the oil molecule (purification). Another result is the production of a more homogeneous mixture of molecules than is present in the entering stock, by preferential rearrangements of the complex molecules (homogenization). The reaction requires but a short time, and is exothermic.

The mixture of oil and gases passes through the exchanger, and is cooled. Then it goes to a separator where the gases pass off, still under a high pressure. The unused hydrogen may be recovered by scrubbing out (oil) the hydrocarbon sulfide and other hydrides, and returned to the entering charge. The hydrogen sulfide may be recovered and by burning it with a limited supply of air, its sulfur recovered as such.

The liquid from the separator is then fed to a fractionating column, and separated into gasoline, gas oils, and residue. The latter is divided into

ALIGNMENT CHART FOR ESTIMATION
OF VISCOSITY INDEX

9-25-3

FIGURE 165.—Viscosity chart for estimating the viscosity index of a lubricating oil, based on the tables of Dean and Davis, *Chem. Met. Eng.*, 36, 618 (1931), corrected for the low viscosities. (Kindly supplied by Dr. E. W. Dean, Standard Oil Development Company.) In order to use chart, find viscosity in Say seconds, at 100° F. (37.8° C.), then for the same sample, at 210° F. (98.9° C.), lay a straight edge to connect the two points on the proper curves, and read numeral under viscosity index. This chart is only slightly different from the one in *Ind. Eng. Chem.*, 23 (1931) (I. Laird Newell)

al fractions (cuts), dewaxed, and subjected to minor treatments, when are ready for the market. No coke is formed during the operation. The lubricant obtained has the five qualities required in a perfect lubricating oil: (1) high viscosity index, (2) low pour point, (3) resistance to oxidation, (4) negligible carbon formation, (5) long life. To this may be added the paraffin-base lubricating oil, which possesses qualities (1), (3), and (5), and naphthenic-base lubricating oils, which possess (2) and (3). By pour point is meant the temperature just below which the oil is thick to pour.



FIGURE 166.—A vacuum distillation tower, which receives the lubricating stock and separates it into several "cuts," preparatory to propane and solvent refining; with its three stripping vessels at its base. (Union Oil Bulletin, Nov., 1934.)

Viscosity Index. To give the viscosity index²⁶ of an oil is a way of rating it with respect to its viscosity-temperature behavior, and it is a method which has become universal. Any oil becomes less viscous as its temperature is raised. A high viscosity index means that this decrease is moderate, no more than should be expected. A low viscosity index means that the oil thins rapidly, so that at elevated temperatures it is like water, and of little value as a lubricant. The temperature index chart (Fig. 165) is based on measurements on two series of oils,²⁷ and on two mathematical expressions.

Vapor-phase Hydrogenation. The hydrogenation of a lubricating oil in the vapor phase is a liquid phase reaction. When gas oil is hydrogenated completely to give gasoline, the reaction takes place in the vapor phase. Hydrogenated gasoline has a high flash point, so that it is less susceptible to explosion than ordinary gasoline. This is "safety gasoline." It is very valuable to the addition of tetraethyl lead, so that a given percentage added

²⁶ "Viscosity variations of oils with temperature," E. W. Dean and G. H. B. Davis, *Chem. Met. Eng.*, 618 (1929). "Alignment chart for estimation of viscosity index of oils," I. Laird Newell, *Ind. Eng. Chem.*, 23, 843 (1931).

²⁷ Series of oils H, moderate decrease in viscosity on heating; series L, considerable decrease.

will produce a reduction in knocking five times that produced in any of the ordinary cracked gasolines.²⁸

Solvent Purification of Lube Fractions. The purpose of the several processes known as solvent purification processes has been the production of an acceptable or superior lubricating oil from an inferior lube fraction. The process might involve the precipitation of the undesirable portions, the extraction and removal of the desirable portions, or both. These processes have gained a well-merited, wide publicity. For illustration, the process employed in California will be sketched.²⁹

Certain western lubricating fractions contain several classes of hydrocarbons. These are as follows: asphaltenes, high-melting thermoplastic solids, low in hydrogen, high in carbon, very undesirable; carbogens, a transition class from asphaltenes to viscous oils, low in hydrogen, high in carbon, undesirable; naphthenes, cyclic compounds of the polymethylene series, more stable than the carbogens, but under severe conditions, sludge forming, undesirable; parathenes, consisting of naphthene rings with para-



FIGURE 167.—At the far left, two propane storage drums; the three vessels in center are part of the de-asphalting plant; at the right, the propane and oil recovery columns. (Union Oil Bulletin, Nov., 1934.)

side chains, the highest type lubricating oil hydrocarbons; paraffins, which resemble parathenes, but with the paraffin side chain predominating, that at room temperatures the higher members are solids, called petrolatum if soft, waxes if hard. On comparing this list with the table for the classification of crudes (Table 55), it will be seen that there is no conflict.

A selection of wax-bearing, naphthenic crudes is made, and distilled in the bubble tower, to give among others a wax distillate fraction. This fraction is again distilled in a plate tower under a high vacuum, giving several cuts, which are then treated separately. The agents are liquid propane at low temperatures, liquid sulfur dioxide, or a liquid sulfur dioxide-benzene mixture (with 25 per cent benzene). Several volumes of liquid propane (a reagent at the ready command of almost any refinery) are mixed with one volume of the lubricating oil fraction; the asphaltic fraction separates and collects as a lower layer, while the propane dissolves the good oil and the wax.

²⁸ Further data will be found in "Hydrogenation of petroleum," R. T. Haslam and R. P. Ross, *Ind. Chem.*, 22, 1030 (1930).

²⁹ *Union Oil Bulletin*, November, 1934, containing "Research behind Triton," Ulrich B. Bray; "From test tube to reality," Earle W. Gard.

The propane-oil layer passes to chilling vessels, where by lowering the temperature, a part of the propane volatilizes, thus reducing the temperature to -40°F. (-40°C.); wax separates. The solution receives fresh liquid propane in order to maintain the original ratio. The chilled suspension is circulated to prevent the wax from settling out; it is finally removed by filtration of the chilled material. The clear oil-propane passes to pre-recovery towers, where the propane is removed by distillation. The residual oil now passes to the solvent treating plant where it meets a sulfur dioxide-benzene mixture which removes the carbogens and most of the paraffenes. Two layers form, with the sulfur dioxide solution of the carbogens and naphthenes the lower one. The parathenes, considered the highest boiling hydrocarbons for lubricating purposes, and the paraffins, form the upper layer, which is passed through a still to remove the small amount of sulfur dioxide it contains; it is bleached by means of granular clay, and is ready for the market. Such an oil is held to have all the qualities of a good lubricating oil should have, and no defects. In the course of purification, about half the original fraction is rejected.

In the Duo-Sol process,³⁰ two solvents operate in a series of 9 pressure vessels and travel in opposite directions. At 9, propane, one of the solvents, laden with paraffins and parathenes, leaves the system to deliver the purified lubricant; fresh cresylic acid (63 per cent cresylic acid with 37 per cent phenol), the second solvent, enters at 9 and travels to 8, 7, until it reaches 1 where it leaves, laden with asphaltenes and carbogens. The residual oil to be treated (thus a $23^{\circ}\text{A. P. I.}$ residual oil from an Oklahoma well) enters at 3. Fresh propane enters at 1. The liquids are moved from one division to the next by means of small, high-speed centrifugal pumps.

Still another process employs "Chlorex," β - β' -dichlorethyl ether, $\text{CH}_2\text{Cl}-\text{O}-\text{CH}_2-\text{CH}_2\text{Cl}$.³¹ Two examples for solvent purification are given

31a

Compare "Refining lubricating oils by solvent extraction," J. V. Hightower, *Chem. Met. Eng.*, 42, 1935; and "The Duo-Sol process," Max B. Miller, *Ibid.*, 285. For a review of the commercial applications of "Chlorex," by W. H. Bahlke, A. B. Brown, *Rocky Oil and Gas J.*, 32, Nos. 3, 60, 62, 72 (1933). See also, "A solvent dewaxing plant," *Chem. Eng.*, 48, 106 (1941), an inset flow sheet.

	Motor Oil, Propane-Refined, SAE-30		Motor Oil, Chlorex-refined, SAE-20	
	Duo Sol. (Max B. Miller)		Without Treatment	With Chlorex treatment
	Before	After		
Gravity	25.7° A.P.I.	29.2° A.P.I.	28.4° A.P.I.	31.1° A.P.I.
Pour point	5° F.	5° F.	5° F.	0° F.
Flash point	420° F.	440° F.	430° F.	420° F.
Fire point	480° F.	500° F.	485° F.	470° F.
Viscosity at 100° F.	590 sec.	552 sec.	380 sec.	298
Viscosity at 130° F.	250	250	177	152
Viscosity at 210° F.	65.5	67	57.5	55
Color A.S.T.M.	53	5 Lt.	6	5.5
Neutralization number03	0	.02	0
Carbon Residue76%	.18	.6%	.3%
Viscosity Index number...	85	100	100	117
O.S. % Sludge.....				
Days 1	0	0	0	0
2	.2	0	0	0
3	1.0	0	1.0	0
4	..	0	..	0
5	..	0	3.5	0
6	..	0	..	0
7	..	0	8.5	0

IMPROVING GASOLINES BY ADDITIONS AND REACTIONS

Gasolines are improved by the addition of foreign substances, by changing the molecule in a definite manner, and by rearranging the molecular structure of the existing molecule, with or without simultaneous reduction of hydrogen. A brief treatment of Diesel oil is included in this section.

Antiknock Compounds. In order to prevent the familiar knock in an internal combustion motor such as in automobiles, and the loss of power which occurs as a result, a number of substances may be added to the fuel with success. The effectiveness per unit weight of these substances varies greatly. The best known antiknock compound is tetraethyl lead, $\text{Pb}(\text{C}_2\text{H}_5)_4$, a liquid which is also the most efficient, for 0.04 per cent tetraethyl lead will retard the detonation as much as does 25 per cent benzene.^{31b} Tetraethyl lead is made by the action of ethyl chloride on a lead-sodium alloy of definite composition, in the presence of a small amount of ethylene bromide.

The antiknock compound is a mixture of 3 parts by volume of tetraethyl lead, a liquid, with 2 parts ethylene bromide; this mixture is added to gasoline, with a small amount of bromonaphthalene, and a red dye (Chapter 28), and the treated gasoline is then retailed. The ethylene bromide is added in order to change the lead oxide formed during the combustion to the volatile lead bromide which passes out with the exhaust gas. The use of gasoline containing tetraethyl lead allows the use of high-pressure motors and thus increases the power efficiency of the fuel. The general use of tetraethyl lead in gasoline was delayed because of the fear that it might prove harmful to health; there is no reason for this fear.³²

There are many other substances which have antiknock properties among others aromatic hydrocarbons such as benzene, and the unsaturated open-chain compounds such as the olefins; therefore, cracked gasoline has long been accepted as superior to straight-run gasoline from class A and B crudes.

The methods of washing the distillate are being modified with the same end in view; the tendency is to do away with the strong sulfuric acid wash and to substitute dilute acids or a different process, as, for example, purification in the vapor phase by fuller's earth.³³ The removal of the unsaturated hydrocarbons is largely prevented by the newer methods of washing.

Iron carbonyl is used to some extent in Europe as an antiknock compound; it has not come into use in America, for it requires frequent cleaning of the spark plugs because of the formation of magnetic oxide in the engine.

There is at the present time no satisfactory theory for the action of an antiknock agent, such as tetraethyl lead. One of the most reasonable, still unestablished, is that the lead compound absorbs certain heat reactions and thus prevents premature combustion.³⁵

^{31b} *Ind. Eng. Chem.*, **14**, 894 (1922).

³² *Public Health Bull. No. 148*, Washington, D. C., 1925.

³³ The Gray process, U. S. Patent 1,340,889; described also in *Chem. Met. Eng.*, **31**, 975 (1922). D. M. Liddell.

³⁴ "Refining of gasoline and kerosene by hypochlorites," Dunstan and Brookes, *Ind. Eng. Chem.*, **11**, 1112 (1922).

³⁵ Compare article by Graham Edgar in "The Nucleus," published by the Northeastern Chemical Society, Rhode Island sections, American Chemical Society, February, 1927, p. 17.

Octane Number. The octane number is the rating of a gasoline as to antiknock properties on the basis of a standard sample consisting of "iso-octane" and normal heptane mixed in various proportions. The older standard was a benzene addition. Normal heptane tends to knock, while "iso-octane," which stands for 2-2-4-trimethylpentane, has marked anti-knock tendencies. By mixing the two in all proportions, a series of fuels is obtained which covers the whole scale of possible gasoline mixtures; such a scale is exact, and reproducible. It is used as primary standard; selected fuels are compared with them and then serve as working standards. So they are cheaper. A gasoline has octane number 70 if on running it in a standard engine, it begins to knock with the same compression ratio which causes a mixture of 70 parts "iso-octane" and 30 parts normal heptane to develop a knock in the same engine under the same conditions. The density and boiling points of "iso-octane" and *n*-heptane are almost identical, an advantage for this purpose.

100-Octane Fuel for Aircraft. Iso-octane itself is not an aircraft fuel. 100-octane aircraft fuel is a blend, and is usually prepared by mixing 40 per cent iso-octane, a selected straight-run gasoline designated as aviation gasoline, isopentane, a very volatile hydrocarbon, and enough tetraethyl lead to reach 100 octane in antiknock rating. An example follows:

40 per cent of 95-octane iso-octane
45 per cent 74-octane aviation gasoline
15 per cent isopentane
3 cu. cm. tetraethyl lead

The gravity of the blend is 69.6° A. P. I., the initial boiling point 100° F. (37.78° C.), the end boiling point 249° F. (120.56° C.), before the addition of lead. The octane rating of the blend before leading is 84.5 by both methods after leading, 100 octane by the U. S. Army Corps Method, 98 octane by the A.S.T.M. Motor Method. The isopentane supplies the volatility at lower temperatures which the iso-octane lacks.

The term "aviation gasoline" as used above indicates the gasoline which serves as the base of the aircraft fuel. The aviation gasoline (base) is generally straight-run gasoline or made by the Houdry process; its boiling point is lower than that of ordinary gasoline; it has good stability, develops a pressure of 7 pounds per square inch at 100° F. (37.78° C.), and shows "acid heat." It may test 65 octane unleaded, 74 leaded.

To illustrate the advantage of high-octane fuel: an airplane which takes 8 minutes to climb to a height of 13,000 feet with 87-octane fuel, will climb to the same height in 5.6 minutes with 100-octane fuel.

Making Pure Iso-octane. One way to prepare the chemical substance iso-octane, more exactly designated as 2,2,4-trimethylpentane, is to dimerize ethylene, and then hydrogenate the resulting octylene. A charging stock of isobutene is selected and sent to the catalyst chamber maintained at 250° to 325° F. [127 to 163° C.] under a pressure of 700 pounds; the product is debutanized and distilled to furnish the iso-octylene fraction. This is then converted to iso-octane by low-pressure catalytic hydrogenation with a nickel catalyst; pressure 75 pounds, temperature 325° F. [163° C.]

	Charge	Product
Gravity	51.4° A.P.I.	51.3° A.P.I.
Octane number (A.S.T.M.)	17.2	77.0
Reid vapor pressure	0.4	8.2
Initial boiling point	222° F.	99° F.
Boiling point 10%	250	174
Boiling point 50%	292	270
Boiling point 90%	367	339
Maximum boiling point	436	368

on from *Chem. Met. Eng.*, 48, April, p. 77 (1941).

Hydroforming Petroleum Naphthas. A new process for "reforming" carbons, and converting low-octane gasolines to high octane has been in successful large-scale operation.* It is a high-temperature, catalytic process, and the action takes place in the presence of hydrogen; yet reforming is not hydrogenation; on the contrary it is dehydrogenation. Part of the hydrogen so produced is recirculated merely to control the extent of the dehydrogenation. The most important property of catalyst is that which causes ring formation and ring closure in molecules which have just undergone partial dehydrogenation. The final product contains a high percentage of aromatic, and a small quantity of aliphatic hydrocarbons, compared with the feed. The product is unusually good and may be blended directly with finished gasoline, after gas removal. Separator followed by distillation in a stabilizing tower.

It is well to have two catalytic reactors so that while one is functioning, the other may be freed of the small amount of coke deposited on the surface of the catalyst granules. The coke is burned off with caution, so as not to harm the catalyst; this is accomplished by adding controlled amounts of air to an inert flue gas. For any given octane level, coke deposition is a function of the amount of recycle gas and its hydrogen concentration. Removal of the coke restores to the catalyst its original activity. The plant at Texas City can reform 7,500 barrels per day of heavy naphthas of 40 or so octane into a product of 80 octane (A.S.T.M.) with a yield of 90 per cent.

Low-octane naphtha side-streams taken from the crude topping system are enriched in aromatics by the process of hydroforming so that they contain 30 to 50 per cent of aromatic hydrocarbons, of which 15 to 20 per cent is toluene. The additional yearly production in this one hydroforming unit alone is 5 million gallons of new toluene which may be separated by distillation. This figure should be contrasted with the 20 million gallons production of 1939 from usual sources, and the estimated yearly total needs of 65 million gallons of toluene.

It has been shown also that adding isopropyl ether to regular gasoline increases the production of 100-octane products,³⁶ and it is expected that this method will be welcomed by many interests.

Polymer Gasoline. The polymerization of olefin-bearing gases has as its object the production of high-octane motor fuel.³⁷ An almost ideal

hydroforming, a new refining process," by D. J. Smith and L. W. Moore, *Chem. Met. Eng.*, 48,

* Standard Oil Development Company, New York.

† Taken in large part from "The thermal process for polymerizing olefin-bearing gases," M. B. R. Swanson, and C. R. Wagner, *Petrol. Inst., Los Angeles meeting* (1935). Also, "New Gulf Refining unit in Port Arthur, Texas, plant," by Ernest Cotton, *Oil and Gas J.*, 37, 25 (1939).

charging stock is the gas formed in a vapor-phase cracking process. The apparatus resembles the cracking plant. The gas enters a furnace coil, to bring it to the reacting temperature, then passes into the reaction coil, somewhat cooler, in which polymerization takes place. Next follows the "arrestor," a small vessel in which a stream of cold oil meets the gas and chills them, in order to stop the action; otherwise an undue amount of tars might be formed. The remainder of the process consists of separating the unchanged or newly produced gases from the liquids; the latter are redistilled, and the gasoline fraction stabilized. The temperature of the furnace coil is 900 to 1000° F. (482 to 538° C.), and the charging gas is compressed to 600 to 800 lbs. pressure (termed low temperature-high pressure polymerization). It is estimated that the 90 vapor-phase cracking plants in the United States produce 100 million cubic feet of gas daily; from which there may be produced 2,730,000 barrels of 78-octane gasoline per year, with much gas left over, as well as other products.

It is estimated that the liquid-phase cracking stills produce 1000 million cubic feet of gas per day, from which there may be produced 30 million barrels of 100-octane gasoline per year. In this case the heating and reaction coils should be at 1,150 to 1,300° F. (621 to 704° C.), and the pressure on the charging stock 50 to 75 lbs. per sq. in.; this would be termed low temperature-low pressure polymerization. The gasoline produced contains from 80 to 85 per cent aromatics, that is, benzene, toluene and the like.

In the computation of prices, if the charging stock is given a value approximating that for heavy fuel oil, since it otherwise possesses only heating value, polymer gasoline can be produced for 5 cents per gallon.

As to natural gas, the washed gas from a natural gasoline absorption system, for example, containing no unsaturated hydrocarbons, would pass through a pyrolysis coil in which unsaturated hydrocarbons (and hydrogen) would form, then a reaction coil, the arrestor, and the separation and condensation apparatus. The natural gas produced in 1933 was 1,555,474,000,000 cubic feet, from which there can be made 77,800,000 barrels of 104-octane gasoline. The polymer gasoline from these various sources would be not far from 100 per cent of the 1936 regular gasoline production. From 1000 cubic feet of gas 2.4 to 4.4 gallons of high-test gasoline will be produced; by passing the residual gas through a second or third time, some more gasoline can be obtained. It may be worth while to indicate that the gas after the first pass will contain 40 per cent hydrogen, and therefore it invites consideration as a source of hydrogen for synthetic ammonia.

There are several plants in operation at the present time (1942).

Processes using solid catalysts have also been developed. In one of these, the catalyst is solid phosphoric-acid, and the gases are heated to about 450° F. (232° C.) under a pressure of 200 lbs.³⁸

Butane is a gas at 26° F. (-3.3° C.) and atmospheric pressure; it has been produced in large quantities and may be transported in liquid form by tank car, truck, and pipe line from East Texas to the Gulf, and from Texas to St. Louis, Mo.; in 1940, its sales were 77,056,000 gallons (60

³⁸ "Polymer gasoline," Gustav Egloff, *Ind. Eng. Chem.*, **28**, 1461 (1936).

or tetraoctet, for domestic gas and enrichment of artificial gas, for enrichment,³⁹ and for manufacturing butadiene for synthetic rubber.⁴⁰

TABLE 57. Cracking stock for polymerizing plants, for the production of high-octane gasolines* (In moles per cent).

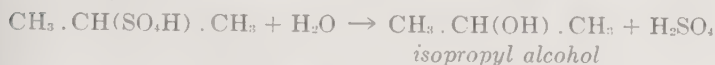
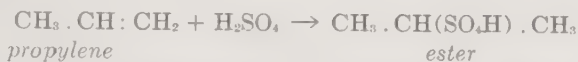
	Gyro vapor-phase gas (2 samples)		Stabilizer overhead discharge (2 samples)		Natural gas d1	Same natural gas after pyrolysis d2
1.	32.5	37.9	0.5	1.2	70.5	H ₂ =11.5{ CH ₄ =62.5{
.....	23.9	25.6	9.2	7.1		15.7
.....	13.4	13.8	8.3	7.8	12.7	5.1
.....	16.8	16.8	40.3	37.6		2.5
.....	4.9	3.1	10.4	11.6	10.3	1.2
.....	6.1	2.8	28.4	30.5		1.5
and up	2.4		2.6	3.4	6.5	0.59
grav. (air=1) ..	1.035	.95			.645	

(1 cu. ft. of d1 besides producing gasoline, left behind 0.91 cu. ft. of new gas d2.)

* Thermal process for polymerizing olefin-bearing gases," M. B. Cooke, H. R. Swanson and Wagner, Sixteenth Annual Meeting, Los Angeles, American Petroleum Institute, 1935.

Cetane Rating. For Diesel oils, a system of rating analogous to the rating for gasoline has been established. The best Diesel fuel is the straight-chain paraffin, normal cetane, C₁₆H₃₄; the worst is α -methyl naphthalene, just the opposite from the gasoline fuels. Mixtures of these two heptanes serve as standards, and the cetane number is the percentage of cetane in a mixture with α -methyl naphthalene which gives the same ignition performance (measured in direct ignition lag) as the fuel tested. For Diesel fuels, a cetane number of 30 gives a good performance, while for the Diesel engines, a lighter fuel testing 40 to 60 cetane is chosen.⁴⁰ The Diesel fuel comes from a gas oil cut from a class A or B crude.

Petroleum as a Raw Material for Alcohols. The cracking of heavy hydrocarbons may be so directed that unsaturated hydrocarbons of low molecular weight, such as ethylene, C₂H₄, propylene, C₃H₆, and butylene, C₄H₈, may be produced; these may be dissolved in sulfuric acid and the esters so formed may then be hydrolyzed, giving the corresponding propyl, or butyl alcohols, as well as others. Both the gases and the sulfuric acid are cooled, and the absorption may be performed under pressure in a series of absorbers which allow a separation at the same time. The temperature may be -20° to 0° C.; a low temperature is sought so that the polymerization into larger molecules is thus prevented. The saturated sulfuric acid liquors are diluted by 3 volumes of water, an undissolved oil layer is removed, and the acid liquor heated in a lead-lined steel still; the alcohols distill over. Example:



and Gas J., 34, No. 34 (Jan. 9, 1936).

Butadiene calls for few departures in equipment or processing," by J. V. Hightower, Refiner,

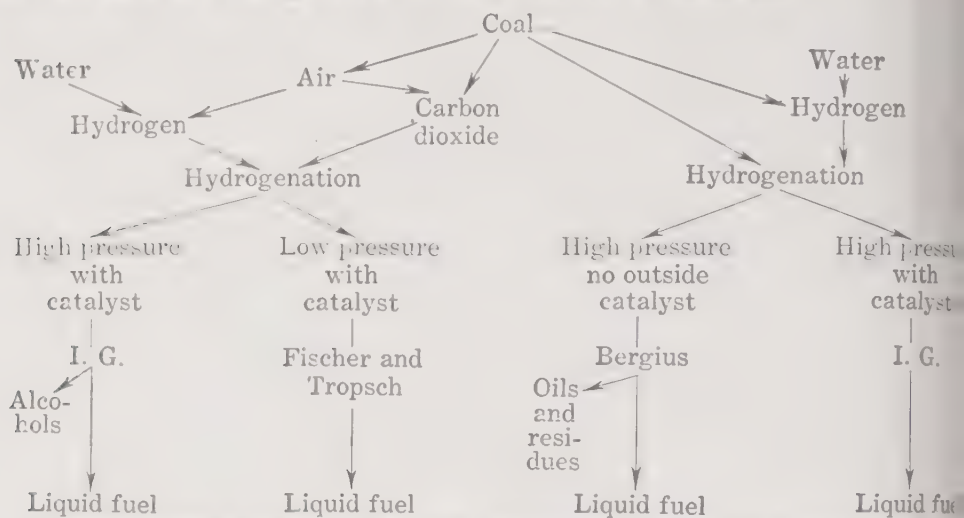
2) "Cetane number study of Diesel fuels" by Ainslie, Young and Hamilton, S.A.E. National Fuel Engineers Meeting, Tulsa, October 23, 1941. "Aniline number and ignition quality," by H. D. Diesel Power, 19, 614 (1941). More on Diesel oils in Appendix.

It is interesting to note that the water molecule which enters the reaction distributes itself in such a way that the hydroxyl ion becomes attached to the carbon having the least hydrogen. As a result, secondary and tertiary alcohols form, and no primary, except in the case of ethylene.

Instead of hydrolyzing, chlorination may be performed and a different series of products obtained, such as dichloroethylene. Regarding the use of a pentane fraction, see Chapter 20.

OTHER SOURCES OF MOTOR SPIRITS

When the supply of crude oil gives out, the chemical engineer will turn to one or more of the other sources of motor spirits which have been developed in the recent past.⁴¹ Motor benzene from the high-temperature distillation of coal has been discussed in Chapter 14. The complete liquefaction of coal by hydrogenation at rather low temperatures and high pressure, the method of Bergius, will yield about 40 gallons of motor spirits per ton of coal, besides 50 gallons of Diesel oil, 35 gallons of fuel oil, and 10,000 cubic feet of gas. In this process⁴² the powdered coal is mixed with oil from a previous run to form a thick paste and heated to 400° C. (752° F.) in an atmosphere of hydrogen under the pressure of 150 atmospheres. In the I.G. process, the coal is hydrogenated in the presence of catalysts.



Tabular view of processes for the liquefaction of coal by hydrogenation.

In England, the hydrogenation of bituminous coal, and of tar produced from by-product coke ovens and coking retorts for city gas plants, is an established process; it is expected that there will be produced annually 15 million imperial gallons of motor fuel from coal, and 15 million gallons more from various tar products.⁴³ Since gasoline is 85 per cent carbon and 15 per cent hydrogen, while coal has only 5 parts hydrogen for each 100 parts carbon, hydrogen to the extent of 10 parts per 90 parts of coal must be introduced. The process is a coal-in-oil phase which is pumped to the converter.

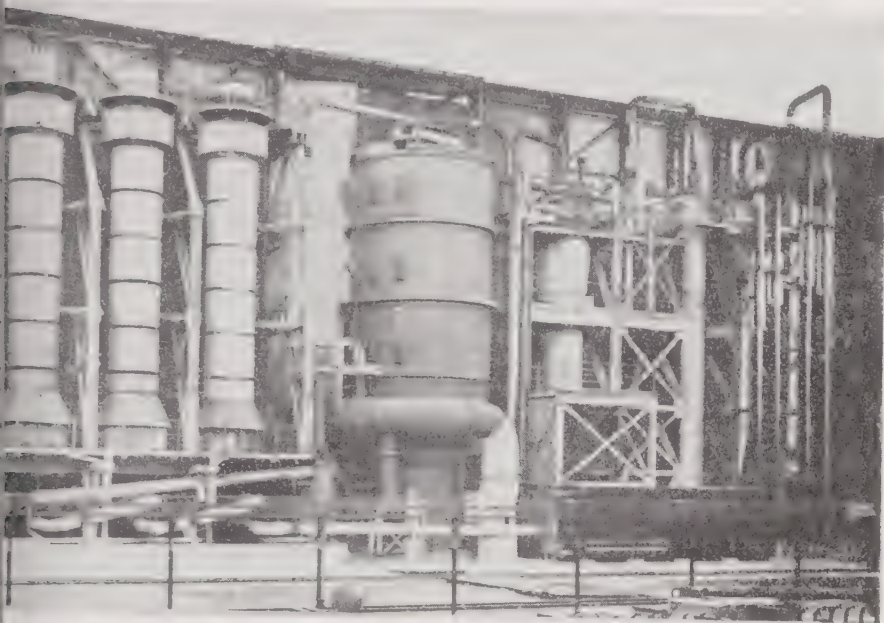
⁴¹ "Future trends in automotive fuels," A. C. Fieldner and R. L. Brown, *Ind. Eng. Chem.* 1009 (1926).

⁴² U. S. Patent 1,592,772, to Friedrich Bergius.

⁴³ "Coal hydrogenation at Billingham," *Chem. Met. Eng.*, 42, 658 (1935), with 7 illustrations on 2 flow-sheets. See also "Oil," by F. Heron Rogers, Presidential Address, *Trans. Institution C. Eng.* (London), 18, 10 (1940).

pressure; the temperature is raised to 390°C . (734°F .) for half an hour, then to 450°C . (842°F .) for one hour. The product is separated into a heavy oil portion, which is hydrogenated further, the motor fuel fraction, and unreacted coal (5 per cent).

Synthetic motor fuel is methanol, made catalytically from carbon monoxide or dioxide with hydrogen. By changing the catalyst, the same materials yield a mixture of higher-boiling liquids which would be suitable for motor spirits; it is called Synthol.



166.—A view of a unit in the coal and tar hydrogenation plant at Billingham-on-Tees, England. At the left, 3 converters in which the paste-in-oil receives hydrogen under pressure; in the center, the pre-heater; next, a gas-liquid separator. To the right, heat exchangers. The brick wall behind the unit is for the protection of the rest of the plant, in case of fire. (By courtesy of the Imperial Chemical Industries, Fertilizer and Synthetic Products, Ltd., Billingham Co., Durham.)

Industrial alcohol has been discussed in Chapter 20, and is suitable if mixed with petroleum distillates and blending agents. Alcohol alone may be used, but a special carburetor is required. Alcohol with 33 per cent sulphur ether, however, is suitable for the regular gasoline carburetor, after coating its float with an alcohol- and ether-resisting skin. Such a motor has become of importance in warm countries, where molasses is available at a low price. Part of the alcohol is changed into ether, as explained in Chapter 30, and plants with continuous operation and a capacity of 3000 gallons daily are in operation. A small amount of a basic denaturant such as pyridine is part of the formula. The "alcolete" of Cuba is such a motor

shales are still another possible source.⁴⁴

"Petroleum and its products," by R. H. McKee, New York, Chemical Catalog Co., Inc. (Reinhold Publishing Co., 1925).

LUBRICANTS

The lubricating oils now in use are mainly mineral oils refined described under paraffin distillate. Blends of mineral and fatty oils, vegetable or animal, are used to a considerable extent, particularly in engine oils in the machine shop. Soluble cutting oils are emulsified with water and cool as well as lubricate; they contain sulfonated oil with mineral oil. Formerly castor, lard, coconut, olive, and many other oils were used with mineral oil additions; several fatty oils are still in great demand for blended lubricating oils, rape oil for example.

The thickest oil obtained from the paraffin fraction may serve for steam cylinder oil, but it usually is blended with fatty oils for such service. Lubricating agents of still higher viscosity are the greases, a calcium soap jelly emulsified with much mineral oil, and usually containing a little water. Graphite by itself and mixed with greases is a lubricant. An outline for the preparation of such a mixture will serve for the preparation of greases in general, although only one grease in a hundred contains graphite.

Tallow is pumped (melted by steam lines) into a kettle 10 feet high and 6 feet wide, fitted with slowly rotating, scraping agitators; the kettle is steam-jacketed and of cast iron. A high-grade hydrated lime is added in an amount sufficient to form the calcium salt of the fatty acids in the tallow; the glycerin formed⁴⁵ at the same time is not removed. When the soap is formed, warm mineral oil in which the graphite has previously been suspended is poured in and the whole mass well mixed; while warm it is comparatively fluid. It is run off from the bottom of the kettle to barrels or cans on a lower floor. The content of calcium soap varies from 10 to 15 per cent, of graphite 2 to 5 per cent (occasionally more up to 25 per cent), of water 1 to 3 per cent, and the balance mineral oil. The grade of oil would pass through the Saybolt viscosimeter⁴⁶ in 150 seconds at 100° or 37.80° C. (60 cc.); this would be an average. The variation, to meet various demands, is from 100 to 200 seconds. A sodium soap jelly has been preferred when heat from the outside may reach the lubricated parts.

Wagon axle grease and railroad curve grease are made by the same reaction of rosin oil⁴⁷ and hydrated lime previously suspended in mineral oil. The hard locomotive cup grease, which must be turned down with a wrench, is made by mixing tallow and oil and pouring in a concentrated solution of caustic soda. The reaction takes place in the cold;⁴⁸ the mass sets to a solid.

A distinction can be made between hand lubrication, cup lubrication, and bath lubrication; the automobile motor has circulating bath lubrication. Lubricants are used to form a film on a rotating metal (shaft) which in turn rests on the stationary bearing; the shaft is really carried by the film. The film must not break; it must have body enough not to be squeezed out by the load; and it must have these properties at the temperature at which it works. In general the viscosity is a measure of the lubricant.

⁴⁵ Chapter 32.

⁴⁶ "Standard methods of chemical analyses," W. W. Scott, New York, D. Van Nostrand Co., 1918.

⁴⁷ Chapter 31.

⁴⁸ See "Lubricating greases," by E. N. Klemgard, New York, Chemical Catalog Co., Inc. (Reinhold Publishing Corp.), 1937.

49 Paraffin-base lubricating oils are improved by mixing with them
cent of Parafflow.⁵⁰
The production of refined petroleum products is given in Table 58.

TABLE 58.—*Production of the major refined products from crude oil, in thousands of barrels of 42 gallons, except for wax, which is given in thousands of pounds.**

	1940
Motor fuel	616,359
Kerosene	73,882
Distillate fuel oil	183,304
Residual fuel oil	316,218
Lubricating oil	36,765
Wax	513,240

Minerals Yearbook, 1940.

The following prices are from miscellaneous sources but will serve as
in estimating the relative money value of petroleum products: crude
California-Long Beach, 27° A. P. I., \$1.05 a barrel; lubricating oil, 14.5
a gallon; kerosene, 10 cents a gallon; regular gasoline, 4.8 cents a gal-
lunker oil, \$1.20 a barrel; all prices are for bulk, and for early 1942.
In 1940 the amount of crude petroleum run to stills amounted to 1,294,-
00 barrels, and these were made into finished and unfinished products
shown below.

TABLE 59.—*Percentage yields of refined products (U. S. 1940).**

Finished products	Per cent (based on crude)
Gasoline	43.1
Kerosene	5.7
Distillate fuel oil	14.2
Residual fuel oil	24.4
Lubricating oil	2.8
Wax1
Coke6
Asphalt	2.3
Road oil6
Still gas	5.5
Other3

Balance, unfinished products and shortage

Minerals Yearbook, 1940.

Tests for Petroleum Oils. Special tests are used for oils. Gasolines
tested for their boiling range to the very last drop (the final temperature
is the dry point), and for their octane number. Gasoline and kero-
sene both tested for specific gravity, color, and clarity. Any oil to be
used as fuel oil is tested among other ways for its heat value, in a calori-
meter. Diesel oils are tested for the cetane number, in addition to the usual
tests. Lubricating oils are tested for their viscosity especially; in the
viscosimeter, the time required for a definite volume at a certain
temperature to pass through a standard orifice is recorded. Viscosities for
different temperatures give the viscosity index. The flash point is the
temperature at which an oil vapor with the surrounding air forms a
mixture which flashes when a small pilot light is applied; the flash test is

for theory of lubrication, see "The technical examination of crude petroleum, petroleum products,
and gas," W. A. Hamor and F. W. Padgett, New York, McGraw-Hill Book Co., 1920, p. 119
S. Patent 1,815,022, or *Ind. Eng. Chem.*, 23, 1452 (1931).

performed especially for kerosene and lubricating oils. There are many other tests which are described in chemical handbooks and in textbooks on analytical chemistry.

Ozocerite. Ozocerite is a mineral wax which occurs in Utah, Colorado and in Galicia; it is of petroleum origin. It may be purified in any one of a number of ways: extraction with solvent, melting and running through charcoal, or heating in contact with fuming sulfuric acid. The original black color is removed, and a yellow wax is produced, which by a special treatment may be made white, and is used under the name of ceresin. In still another process, the crude wax is distilled with superheated steam, yielding a white wax melting at 140° F. (60° C.), light oil, a semi-solid wax used in the perfumery industry, and a black residue. The latter mixed with raw rubber and vulcanized forms Okonite, a flexible, tough, waterproof insulator.

Asphalt, Tar, Road Oil. The production of petroleum asphalt, tars and oils as shown below will indicate the importance of the material. Figures on native asphalts which include gilsonite are included.

TABLE 60.—*Production of asphalts and road oils in the United States in 1940*

Native asphalts and related bitumens*.....	490,665 short tons
Petroleum asphalt*	5,346,700 " "
Road oils	
Liquid asphaltic road oils†.....	608,914,551 gallons
Other road oils†	252,857,527 " "
Tar or residuum	52,029,686 "

* Minerals Yearbook, 1940.

† Bureau of the Census.

Native asphalts are solid bitumens (that is, hydrocarbons) which melt on heating to the temperature of boiling water, or near it. Trinidad Lake asphalt is a solid bitumen found naturally mixed with silica and clay and occurs in just that form only on the island of Trinidad. Other asphalts are found impregnating amorphous limestone, crystalline limestone, or shales in Europe (Sicily and other localities), in Oklahoma, Utah, and California. The asphalts are used for paving roads, and for this purpose are frequently softened by the addition of residues from the distillation of various crude oils.

OTHER PATENTS

U. S. Patent 1,848,054, dewaxing petroleum fractions by filtering under different pressure; 1,800,887, breaking petroleum emulsions; 1,814,042, continuous transformation of petroleum hydrocarbons into gasoline and coke-like complexes, without the formation of fuel oil; 1,848,681, antiknock gasoline, by cracking oils at high temperature; 1,838,449 and 1,768,521, absorption of gasoline from natural gas, by oil scrubbing; 2,074,338, a lubricant comprising in combination a mineral oil and a halogenated fatty acid of the aliphatic series; 1,937,759, on the art of refining; Canadian Patents 339,404, wax separation from oil; 339,405, hydrocarbon oil stabilization; U. S. Patents 2,032,666, stabilization of light hydrocarbon oil and particularly pressure distillation; 2,032,662, desulfurizing gasoline; 2,032,680, process of varying the bitumen content of rock asphalt; 2,038,599, 2,039,259, carrying out catalytic reactions, to M. Pier P. Jacob; 1,946,108, production of catalysts; 2,068,979, method of preventing corrosion in oil stills, by adding an oil soluble naphthenate; 1,955,272, on the recovery of aluminum chloride from the residue of aluminum chloride refining; 1,955,260, to produce "synthetic lubricating oils" from paraffin wax, cracking, then polymerizing with catalysts, followed by an aluminum chloride treatment; 2,069,170, refining and lubricating oil by propane vapors; 2,069,173, refining hydrocarbon gases, with catalysts.

of the oil is separated from saturated. British Patent 442,429, use of an electrical current to separate asphalt from the oil. U. S. Patent 2,038,798, furfural as solvent. 2,027,346, propylene dichloride and ethylene glycol ether as solvent and used the wax. 2,028,361, phenol, aniline, and other selective solvents; 39,441, benzene as precipitant of the asphaltic impurities; other patents use of certain solvents for the purification of lube stock are 2,054,433, 2,055,428, 2,047,826, 2,041,885, 2,043,389; also Canadian Patent 343,452; U. S. Patent 1,622,223, heat exchange apparatus; 2,217,703, catalytic conversion of hydrocarbons.

PROBLEMS

A storage tank for gasoline, with closed top equipped with a patent breathing valve, is 60 feet circular in diameter and 40 feet in height. It is designed for gasoline having a gravity of 55° A.P.I. at 60° F./60° F. How many gallons will it hold? How many gallons of height? A table of A.P.I. degrees and corresponding specific gravity will be found in the appendix.

In a "bulk plant," there is a storage tank 35 feet high, 25 feet in circular diameter, for the storage of kerosene of 40 A.P.I. at 60° F./60° F. How many gallons will it hold, and how many gallons for an inch of height?

In the same "bulk plant," another cylindrical tank is 25 feet in diameter and 12 feet in height. It holds a fuel oil testing 36 A.P.I. at 60° F./60° F. What is the capacity of the tank for this oil, and how many gallons per inch will it hold?

A pipe line delivers 5500 barrels of oil to a refinery in one day, at a regular rate of 24 hours. The line is an 8-inch line. The oil is stored in 3 receiving tanks which are circular in cross-section, and 12 feet high. What size will the tanks have to hold one day's delivery? What is the velocity of the oil in the pipe, in feet per second? $\text{Velocity} \times \text{area} = \text{discharge}$.)

From the table of "Percentage yield of refined products" in the text, which gives weight relations, take the figures for each year and tabulate how much refined product by weight you would have produced every day from a daily crude input of 100,000 barrels. For the gasoline, kerosene, and fuel oil lines, compute the volume, using the A.P.I. densities as given in problems 1, 2, and 3.

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There was a time not so long ago when the chemist sought exclusively for natural products so that he might extract or distill from them the complicated molecules containing carbon, hydrogen, and oxygen or nitrogen. The distillates or extracts were chemicals originating in nature's laboratory in living systems, vegetable or animal; they were therefore called "organic." It was with reverence that the chemist isolated such chemicals. Today he is bolder. Natural sources are still sought and utilized, but in addition the chemist or engineer uses coal and limestone, for example, and produces from them the delicate and volatile acetate esters. This makes true the saying: From rocks to ethereal solvents. But it is well to note at once that in these bold syntheses, all the worker does is to provide the circumstances and conditions so that the laws of nature may function to his advantage. At no time does he make nature do his will; the achievement is rather the discoveries of a few of those laws; the attitude of humility before the increasingly mysterious laws of nature is still in order.

Chapter 25

Synthetic and Semi-Synthetic Organic Chemicals

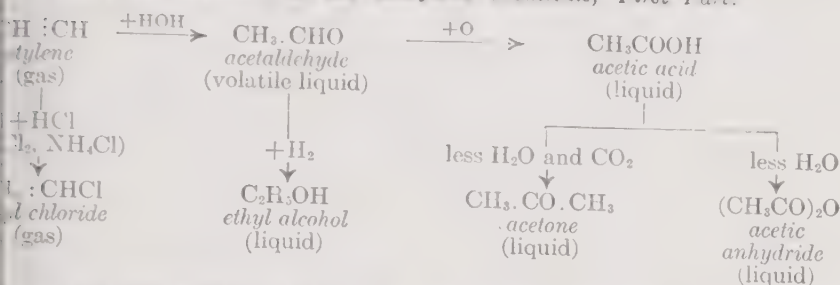
In the course of the first four decades of the twentieth century, particularly since the war of 1914-18, many synthetic organic chemicals have been brought to the commercial state and have entered the economic life of the world. The best known are the compounds derived from acetylene; by catalytic hydration, acetaldehyde is formed, and this in turn by catalytic oxidation, yields acetic acid. This is synthetic acetic acid, used to replace in all its uses the older acetic acid from wood distillation. More recent date, and perhaps less well known, are the chemicals built up from ethylene, $\text{CH}_2 : \text{CH}_2$, as starting material; they include ethylene glycol and the glycol ethers. The ethylene derivatives are manufactured mainly by straightforward chemical reaction, and only in rare instances by contact catalysis. If it had not been for this important group of ethylene derivatives, this chapter might have been entitled: Organic Contact Catalytic Processes. A third important starting material is carbon monoxide, which reacts with hydrogen, in contact with a properly chosen catalytic agent, to form methane, CH_4 , or methanol, CH_3OH , and higher alcohols, according to the nature of the catalyst and other conditions.

The three series listed in the previous paragraph represent synthetic chemicals. What might be called semi-synthetics are chemicals resulting from partial or controlled oxidation of natural products, chiefly again with the aid of a contact substance; for example, phthalic anhydride from naphthalene. Another semi-synthetic group would be the hydrogenated vegetable oils which become "vegetable fats," because of the addition of hydrogen to the molecule.

A number of synthetic and semi-synthetic substances, of value in the perfume industry, are described in Chapter 30. Synthetic amyl alcohol and pentane is included in Chapter 20.

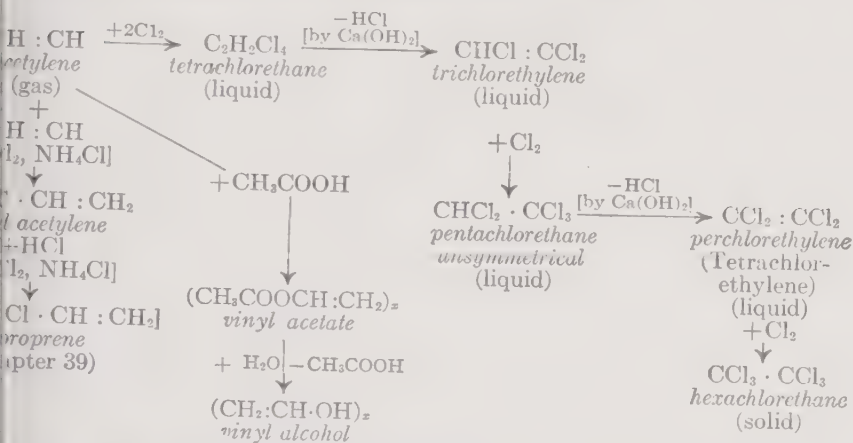
CHEMICALS BASED ON ACETYLENE AS STARTING MATERIAL

Acetylene is the gas formed by the action of water on calcium carbide, or by the action of the electric furnace. The early use of the gas was as an illuminant, about 30 years ago, when its dazzling white light was highly prized.

TABLE 61.—Relation of the acetylene chemicals,¹ First Part.

The heat of combustion led to its use in welding and cutting torches. Acetylene was generated and fed into a suspension of mercurous sulfate in water and sulfuric acid, where it is a chemical, which attaches a molecule of sulfuric acid to each one of its molecules, to form acetaldehyde. By oxidation, acetic acid is then formed, and this in turn may serve as a source for acetone. Hydrogenation, acetaldehyde gives ethyl alcohol, an actual source of

TABLE 62.—Relation of the acetylene chemicals, Second Part.



material. The relation between acetylene and the products based on it are given in Tables 61 and 62.

Acetaldehyde. Acetylene^{1a} is generated from calcium carbide by the action of air-free water in a series of generators feeding a central holder. The gas from the holder enters the reaction vessel made of Duriron, conical in shape, and surmounted by a short plate column. A quantity of liquid

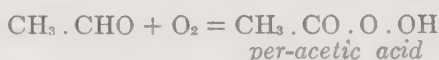
for the synthesis of acetic acid from acetylene was worked out for large-scale operation by a group at Shawinigan Falls, Ontario, Canada, during the war emergency of 1914-18 and had as its object the manufacture of acetone, required in the production of munitions. A survey of the literature will be found in "Synthetic acetic acid and acetone," J. T. Rooney, *Chem. Met. Eng.*, 1919. For other sources, see brief statement in Chapter 19.

is contained in the cone bottom of the reaction vessel, and contains acetaldehyde, and mercurous sulfate in suspension. The gas enters at the bottom at a steady rate and keeps the thin sludge well stirred. At a corresponding rate, air-free, lukewarm water is fed in. At definite intervals a part of the sludge is removed, and a charge of fresh mercurous sulfate suspended in air-free water is supplied. The reaction $C_2H_2 + H_2O = CH_3CHO$ is exothermic, so that heat must be removed by cold water circulating in a coil placed in the reaction vessel. The temperature is maintained at $68^\circ C.$ ($154^\circ F.$) at which acetaldehyde passes out freely, carrying with it a certain amount of water vapor. In the plate tower, cooling causes condensation of a water solution of aldehyde, which becomes stronger higher the plate. Acetaldehyde, water, acetylene, and several other reaction products in smaller quantities pass out at the top; the vapors rise upward in a circular box with cooling coils. A water solution of acetaldehyde containing about 20 per cent water is collected and stored in aluminum tanks; the acetylene gas passes out and after purification joins the main gas on its way to the reaction vessel. Pure acetaldehyde boils at $20^\circ C.$ ($68^\circ F.$) at atmospheric pressure. There were produced in the United States in 1940 201,484,831 pounds of synthetic acetaldehyde.

Acetic Acid. From acetaldehyde directly, several chemicals are formed: acetic acid, ethyl acetate, butyl acetate, acetic anhydride, while acetylene and acetylene may be made to yield acetic anhydride, all by catalytic reactions.

For acetic acid, a batch process² is used. A thousand gallons of acetaldehyde from the acetylene hydration, rectified so that its water content is very low, are pumped into an aluminum-lined reaction vessel provided with cooling coils for water or steam. To this 0.5 per cent manganese sulfate or acetate is added, and air (300 cu. ft. per minute) blown in against the pressure at which the reaction vessel is operated, about 3 atmospheres. The temperature is raised to $25^\circ C.$ ($77^\circ F.$), which is below the boiling point of acetaldehyde at the pressure used. As the reaction gets under way, the temperature rises to $65^\circ C.$ ($149^\circ F.$) and the pressure to 75 pounds: $2CH_3CHO + O_2 = 2CH_3COOH$. Nitrogen is allowed to escape through a liquid-cooled separator, which retains the entrained aldehyde and acid. The reaction is complete in 8 to 12 hours, when the charge is distilled, then rectified with the aid of a plate column, operated continuously and yields 99 per cent acetic acid.

The function of the manganese catalyst is not to catalyze the oxidation of the aldehyde, but rather to decompose an intermediate product, peracetic acid, which is explosive; as it decomposes, the desired acetic acid is formed. The higher manganese oxide formed attacks fresh acetaldehyde:



² English Patent 132,558 (1918), class II, 3, p. 91 abridgements; 132,557 (1918), class II, 3 abridgements.

Ethyl Acetate from Acetaldehyde. In the presence of small amounts of aluminum ethylate, $\text{Al}(\text{C}_2\text{H}_5\text{O})_3$, and aluminum chloride, AlCl_3 , acetaldehyde is transformed to ethyl acetate with a recovery of over 90 per cent: $\text{CH}_3\text{CHO} + \text{CH}_3\text{COOC}_2\text{H}_5$. At the present time, ethyl acetate is made exclusively from fermentation alcohol and acetic acid from various sources, but the process just given may gain industrial importance in the

Acetic Anhydride from Ethylidene Diacetate. If instead of passing acetaldehyde into a water suspension of mercurous sulfate, as is done in the present process in this series, it is passed into a suspension of mercurous sulfate in concentrated or glacial acetic acid, using the same kind of reaction vessel, there is formed ethylidene diacetate. (The ethylidene group is $\text{CH}_3\text{CH}:$). $\text{C}_2\text{H}_2 + 2\text{CH}_3\text{COOH} = \text{CH}_3\text{CH}(\text{O} \cdot \text{CO} \cdot \text{CH}_3)_2$.

On distilling this product in the presence of small quantities of anhydrous salts or agents, such as zinc chloride or sodium pyrophosphate, $\text{Na}_2\text{P}_2\text{O}_7$, the diacetate decomposes into acetaldehyde and acetic anhydride: $\text{CH}_3\text{CH}(\text{O} \cdot \text{CO} \cdot \text{CH}_3)_2 = \text{CH}_3\text{CHO} + \text{O}(\text{CO} \cdot \text{CH}_3)_2$.

The distillation may be performed at reduced pressure (100 mm.) and temperature (176° F.), or at atmospheric pressure and 130° C. (266° F.). The acetaldehyde may be used over again in the acetic acid synthesis.

It has been found advantageous to introduce the decomposing agent, sodium pyrophosphate, in small lots³ at suitable intervals into the boiling acetaldehyde acetate, in order to avoid forming acetic acid or tars. The conversion is 87.4 per cent. In the subsequent distillation, unchanged ethylidene diacetate is left behind; the distillate is fractionated and furnishes 80 per cent acetic anhydride, the customary commercial strength.

Acetic Anhydride from Acetic Acid. Acetic anhydride may be made from glacial acetic acid by passing it in vapor form over granules of catalyst⁴ kept at 600° to 620° C. (1112° to 1148° F.). The catalyst is prepared by mixing 200 grams of sodium ammonium phosphate, $\text{NaNH}_4\text{HPO}_4$, with 100 grams of boron phosphate; the yield is 48 to 50 per cent. The standard method for acetic anhydride manufacture will be found in Chapter

on the production of synthetic acetic acid in the United States in 1940, 364,384 pounds. (See also Chapter 16).

Chlorinated Hydrocarbons. By the chlorination of acetylene to tetrachloroethane, followed by the removal of hydrogen chloride, trichloroethylene is formed. It is a liquid which has become an important solvent. It is now made at the rate of many tons a day. By chlorination, with subsequent hydrogen chloride removal, and again chlorination, three more chlorinated hydrocarbons are formed, as shown in Table 62.^{4a}

Another important branch of the acetylene chemicals family is the vinyl compounds. A stream of acetylene in acetic acid gives *vinyl acetate* which can be polymerized to various degrees, after which it is hydrolyzed to

³ Patent 1,578,454.

⁴ Patent 1,870,357.

^{4a} Compare "An R. & H. Technical Bulletin," "Chlorinated Hydrocarbons," (1935), The R. & H. Chemical Department, E. I. du Pont de Nemours and Co., Wilmington, Del.

uses. Acetylene to form chloroprene, 2-chlor-1, 3-butadiene, is treated in Chapter 39.

Degreasing Metal Surfaces. An important use of certain of the newer solvents is in the degreasing of metal surfaces, preparatory to coating them with another metal, by electrolysis, by dipping, or in some other way. Triethylene particularly is favored, and not only its uses, but several methods for performing the degreasing, with the apparatus, have been the subject of patents.^{4b} In one system, the cold metal parts are suspended in a bath of the solvent, which recondenses on the walls of the same vessel, and so to form a short reflux column; only the pure solvent, with maximum efficiency, reaches the objects. The solvent is kept warm by a steam jacket, so the vapors do not escape, thanks to their great weight relative to air. In order to prevent corrosion, a "stabilizer" is added; this may be 0.001 per cent triethylamine,^{4d} 0.05 per cent to 0.1 per cent amylene,^{4e} or, less satisfactory, gasoline.^{4f}

SYNTHETICS WITH ETHYLENE AS STARTING MATERIAL

An important series of valuable organic compounds has been realized, starting from the brilliant work of American chemists and chemical engineers, beginning with the molecule of ethylene, $\text{CH}_2 : \text{CH}_2$. The family tree in Chapter 3 exhibits the relation between the more important members of this series. Ethylene is an unsaturated compound, which readily forms addition

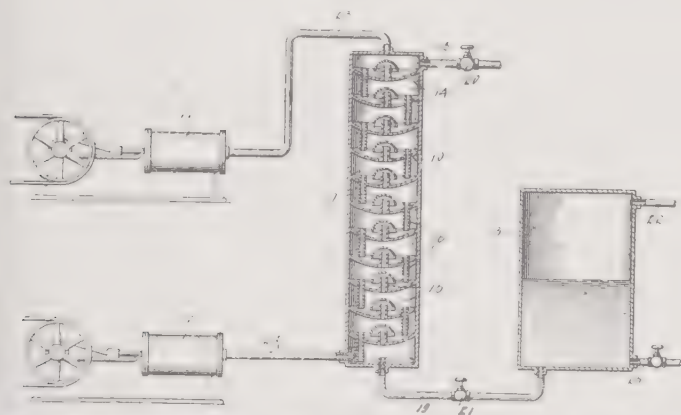


FIGURE 167.—Plant for the extraction of ethylene from a gas mixture, showing absorption tower, separating chamber, and the two compressors. (From the patent.)

The additions which are of service here are hypochlorous acid, followed by reactions which replace the halogen by a hydroxyl group, an ethoxy (OC_2H_5) or other alkyloxy group, or an acetyl radical (CH_3CO), or reactions which remove hydrogen chloride or water. The substance is ethylene glycol, $\text{OH} \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{OH}$, a liquid, manufactured at the rate of 30 tons a day.

Patents 1,906,968; 1,961,867; 1,875,937; 1,938,841; 1,869,845; and 1,869,826.
 Patent 1,911,926.
 Patent 1,904,450.
 Patent 1,816,895.

Ethylene. The gas ethylene is obtained in the large amount required for this industry from oil, cracked in the vapor phase (Gyro), or cracked natural gas; fair quantities are also present in coke-oven gas. Ethylene is obtained in the pure state by compressing the raw gas to several atmospheres and treating this with acetone in an absorption tower (see Fig. 167). Acetone is forced in at the top and travels downward over the plates. The gas travels upward, bubbling through the solvent, in which ethylene dissolves. An acetone solution rich in ethylene collects at the bottom of the tower, and is sent to an expansion chamber, where the pressure is released; the pure gas escapes from the liquid and is drawn off through a line at the top of the chamber. The liquid below is used over again. When maximum production is needed, it is warmed and passed through a plate tower; the residual ethylene is thus recovered. The acetone is then ready for a new absorption cycle. The pure ethylene gas is collected in a holder from which it is drawn as needed.

Ethylene is conveniently obtained from ethyl alcohol, by careful dehydration; this could be the method employed for making mustard (Chapter 34).

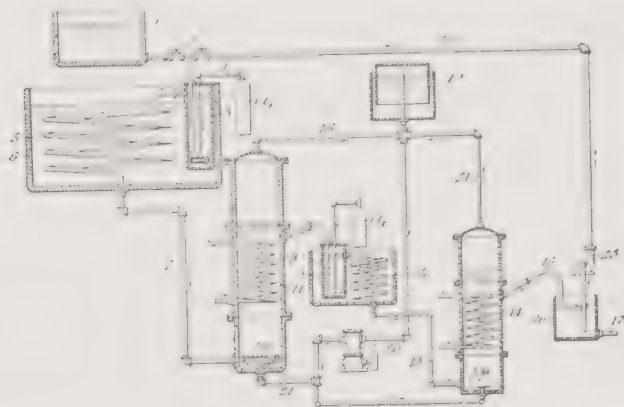


FIGURE 168.—Absorption of ethylene in hypochlorous acid to form the chlorhydrin. 3 and 9, chlorinating cell to form hypochlorous acid; 8 and 10, reaction towers; 10 and 10a, inlets for ethylene gas; 1, storage for sodium hypochlorite solution. (From the patent of J. H. Jones, U. S. Patent 1,422,184.)

Ethylene Chlorhydrin. In the next step, ethylene forms an addition compound with hypochlorous acid, HOCl , in water solution,⁵ the chlorhydrin formed, $\text{OH} \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{Cl}$, remaining also in solution in water. Inasmuch as hypochlorous acid is not stable, its sodium salt, sodium hypochlorite, NaOCl , is prepared, and the free acid liberated at the moment it is to react.

Chlorine gas is passed into a solution of iron-free caustic soda, kept at 10°C . (50°F .), in order to avoid chlorate formation. The reaction $2\text{NaOH} + \text{Cl}_2 = \text{NaOCl} + \text{NaCl} + \text{H}_2\text{O}$ takes place. Enough chlorine is passed in so that no free alkali remains; the strength is adjusted at 5 to 7 per cent NaOCl . The vessel and pipes are of chemical stoneware.

The hypochlorite solution passes to the first decomposing cell (Fig. 168), maintained at 0° to 10°C . (32° to 50°F .), where it meets a stream of chlorine gas in quantity sufficient to react with most, but not

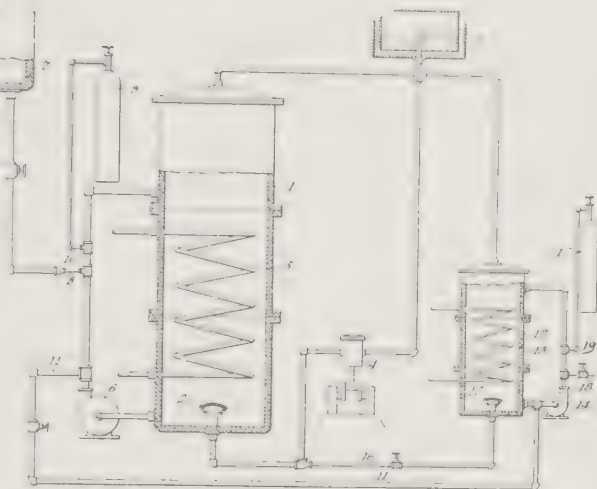
⁵ U. S. Patent 1,422,184.

⁶ U. S. Patent 1,456,916.

sodium hypochlorite: $\text{NaOCl} + \text{Cl}_2 + \text{H}_2\text{O} = 2\text{HOCl} + \text{NaCl}$. The liquid of hypochlorous acid now passes through a cooling coil to the bottom of the first reaction tower (8 in the sketch). Ethylene gas enters through a porous plate in the base of the tower, so that it is divided into fine bubbles. A quantity of liquid several feet in height is kept in the tower, through this, the gas rises, combining with the free hypochlorous acid: $\text{HOCl} + \text{OH} \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{Cl}$. The reaction is exothermic; by means of the coils placed in the tower, brine may be circulated, and this heat used, so that the temperature is maintained close to 0°C . (32°F .).

A portion of the liquid in the tower is allowed to overflow into the second reaction cell (9 in sketch), placed in a brine tank. In this cell a fine stream of chlorine enters and decomposes the remaining sodium hypochlorite; this solution passes through a cooling coil again, and enters the first reaction tower, again forming a body of liquid through which the gas is allowed to rise in fine bubbles. The overflow from this cell reaches an intermediate tank; a portion is sent to join the fresh sodium hypochlorite liquor for the first cell, serving as diluent. The main part is boiled off and purified; the impurities are sodium chloride, a small amount of chloric acid, and traces of hypochlorous acid and of chlorate. A small excess of sodium bisulfite is added to destroy the latter two substances, and calcium carbonate to neutrality. The liquid obtained may contain as much as 20 per cent ethylene chlorhydrin; it is concentrated further by distillation, usually to the 42.3 per cent strength, because this is a constant-boiling mixture.

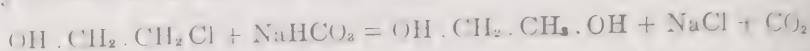
169.—Improved procedure for the absorption of ethylene in hypochlorous acid. In each reaction tower (1 and 12), the chlorhydrin solution is circulated, with injection of small amounts of sodium hypochlorite (8) and of chlorine (at 18 and 19). (From the patent.)



This procedure has been improved ⁷ (see Fig. 169) by circulating a larger portion of the chlorhydrin solution, and injecting only enough sodium hypochlorite solution to produce 0.1 per cent hypochlorous acid in the liquid in the reaction tower; in fact, the customary concentration is 0.06 per cent. One part of hypochlorite solution is added to 80 to 250 parts of diluted liquor. A stream of chlorine sufficient to decompose 50 to 80

per cent of the sodium hypochlorite is injected into the circulating pipe. A definite amount of liquor is discharged constantly and worked up its chlorhydrin content.

Ethylene Glycol. Ethylene chlorhydrin is transformed into ethylene glycol by means of a solution of sodium bicarbonate:



The apparatus⁸ (see Fig. 159) consists of two closed kettles, steam-jacketed and with stirrer, and two storage tanks, one for a caustic solution, one for the chlorhydrin solution. The caustic solution is made 20 per cent NaOH, the chlorhydrin 40 per cent $\text{OH} \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{Cl}$. Caustic solution is run into kettle 2, and carbon dioxide passed in, to form the bicarbonate: $\text{NaOH} + \text{CO}_2 = \text{NaHCO}_3$. A charge of chlorhydrin solution, in amount just right to follow equation (1), is run in, and the temperature is raised to 70° C. (158° F.) while stirring. The reaction starts and proceeds smoothly; it is complete in 4 hours. The gas evolved (CO_2) is passed into kettle 1, which contains its charge of caustic solution, so that bicarbonate for the next batch is being made by the same gas.

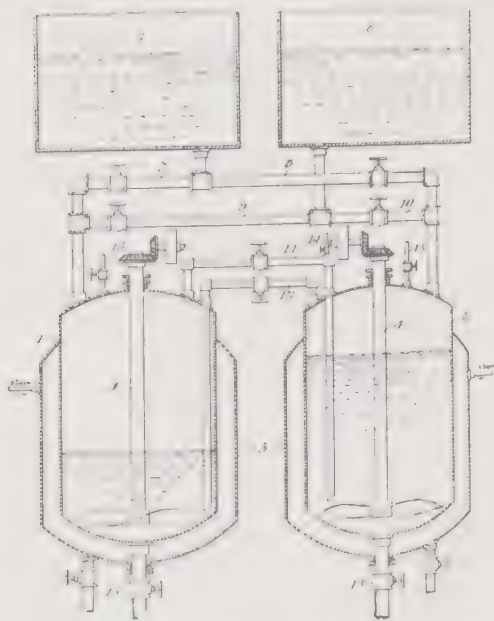


FIGURE 170.—Reaction vessels for making ethylene glycol from ethylene chlorhydrin. Vessel 1 contains the solutions of bicarbonate and chlorhydrin; the gas evolved passes into the cold caustic solution in vessel 2. (From the patent.)

It is necessary to guard against losses in the form of ethylene oxide; these are minimized by starting with the cold caustic.

The weak glycol solution obtained is concentrated by heating under vacuum, water vapors passing out. When completely dehydrated it is a somewhat viscous liquid, very hygroscopic, boiling at 197.2° C. (387° F.). It is miscible with water in all proportions, causing a drop in the freezing point of the solution; 60 per cent ethylene glycol and 40 per cent water has the minimum freezing point, — 49° C. (— 56° F.), hence its value as an antifreeze in automobile radiators.

⁸ U. S. Patent 1,442,386.

second method for making ethylene glycol consists of making ethylene and then hydrating it. Ethylene oxide is formed when the two gases, C_2H_4 , and oxygen, O_2 , are mixed and the mixture passed over a substance consisting essentially of aluminum oxide and silver; the oxide is selectively absorbed from the gaseous mixture.^{8a}

A mixture of 200 parts of air and 5 parts of ethylene is passed over a silver-containing catalyst at 240-260° C. (464-500° F.) with the formation of ethylene oxide.^{8b} (Compare under Glycol Ethers.)

Ethylene Glycol from Ethylene Chloride. Ethylene glycol may also be made from ethylene chloride, $\text{C}_2\text{H}_4\text{Cl}_2$, in a single step.⁹ The following materials in the proportions indicated are placed in a kettle with a closed, jacketed extension which is jacketed, so that its temperature may be regulated.

ethylene chloride	10 parts by weight
soda ash	10 parts by weight
sodium acetate	2 parts by weight
85 per cent ethyl alcohol	15 parts by weight

The kettle is heated to 125° to 175° C. (257° to 347° F.); the pressure is regulated to 150 to 200 pounds by releasing some of the carbon dioxide produced. After several hours, the action is over; the sodium chloride formed is insoluble in the liquor, and may be settled out or centrifuged. The liquor consists of glycol and alcohol, which are separated by distillation.

Ethylene chloride, $\text{C}_2\text{H}_4\text{Cl}_2$, has become an important substance; it is a solvent and also a starting point for chemical syntheses. Among the latter, ethylene glycol is made commercially from the dichloride. It is formed by passing ethylene gas into a cylindrical container in which a contact substance such as activated carbon has been placed. Chlorine gas enters at the top level, and the two gases travel downward; the liquid product is collected in a separator: $\text{C}_2\text{H}_4 + \text{Cl}_2 = \text{C}_2\text{H}_4\text{Cl}_2$. The gases may also be passed into a body of liquid from previous batches, under a layer of oil. The heat of formation of ethylene chloride is considerable (60 calories per gram-mol), and must be removed by cooling coils or a cooling jacket. Ethylene dichloride is also a by-product in ethylene chlorohydrin manufacture.

Ethylene glycol may also be obtained from glycol diacetate,¹⁰ itself made from ethylene chloride by a procedure to be discussed presently. The glycol diacetate, a liquid, is mixed with an alcohol such as ethyl alcohol, and 2 per cent sulfuric acid, and the mixture heated in a Duriron reaction vessel. The acetate passes out and is collected, as it forms a marketable by-product. After neutralizing, the glycol is distilled from the residual liquor.

GLYCOL ESTERS

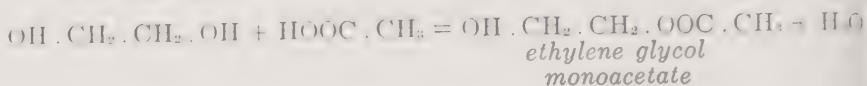
One of the earliest derivatives of ethylene glycol was the acetate ester, which has good solvent properties; since then a number of other

S. Patent 2,125,333.
 British Patent 500,382.
 S. Patent 1,402,317.
 S. Patent 1,454,604.

esters have been manufactured, but the ether-alcohols and the ethers both to be presented in this chapter, have overshadowed the esters. Esters are important intermediate products between ethylene chloride and glycol, for example.

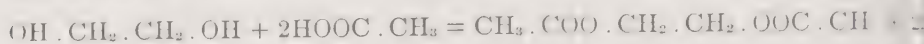
It may be noted that a mono-ester of a glycol is an alcohol ester, the corresponding di-ester would have no alcohol group.

A satisfactory, inexpensive method¹¹ of forming ethylene glycol acetate consists in placing glycol and acetic acid in a boiling kettle (equipped with a vertical extension serving for refluxing a part of the vapors). The temperature is maintained around 100° C. (212° F.); the water formed during esterification is able to escape through the refluxing jacket. Glycol, acetic acid or ester are re-condensed. Any water of dilution introduced with the acetic acid will also pass out, so that it is the special feature of this method that the ester may be produced with weak acetic acid, as 25 per cent acid, a cheaper material than 99 per cent or 99.8 per cent acid. The boiling is continued until the acid is essentially all converted.



The ester is purified by distilling it; any unchanged acid passes over first and then the ester.

The diacetate is formed in the same way, except that twice the amount of acetic acid is placed in the kettle. The reaction then is:



The diacetate may also be made from ethylene chloride, by heating at 160° C. (320° F.) under pressure with sodium acetate and ethyl alcohol as a diluent.¹²

Glycol Nitrates. Ethylene glycol dinitrate is manufactured very much as nitroglycerin is, and it is used as an explosive. Its effectiveness as an explosive equals that of nitroglycerin; its great value is in the manufacture of low-freezing dynamites, as it freezes at -22.8° C. (-9° F.), while glycerin freezes at +13° C. (+55.4° F.). It is less sensitive to shock than nitroglycerin. Diethylene glycol may also be nitrated; the resulting diethylene glycol dinitrate has the low freezing point of -11.3° C. (+11.5° F.), and is used in the manufacture of low-freezing dynamites.

GLYCOL ETHERS

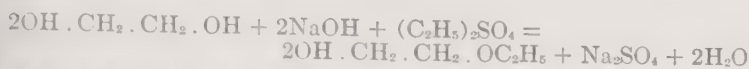
The insistent demand for chemicals which would be good solvents for nitrocellulose stimulated the study of glycol derivatives. It was found that the combination of the ether group with the alcohol group in a molecule should confer superior solvent properties,¹³ because the first solvent for nitrocellulose was an ether-alcohol mixture; neither of the substances alone had any solvent action. This expectation was fully and brilliantly realized. One of the first compounds of this type was the monoethyl

¹¹ U. S. Patent 1,534,752.

¹² U. S. Patent 1,430,324.

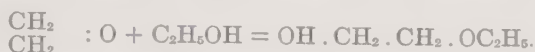
¹³ *Ind. Eng. Chem.*, **18**, 700 (1926).

ylene glycol, $\text{OH} \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{OC}_2\text{H}_5$, sold under the name of Cello-simple and efficient method for its preparation, in a single step, from cheap reagents, is as follows ¹⁴: Ethylene glycol of commercial grade, ethyl sulfate, and caustic soda (crushed solid) in the proportions required for the reaction:



carried in a kettle with reflux tower for 3 hours. After that time, the mixture is vacuum-distilled, leaving the inorganic salt in the still. The residue is redistilled at atmospheric pressure and the recovery is 60 per cent or over. The product is a colorless liquid boiling at 134°C . (273°F .); soluble in water, glycerin, ethylene glycol, amyl acetate and butyl acetate. It is a solvent for gums, resins, and nitrocellulose; it has been used as an extraction agent for essential oils and for flavors and perfumes. This product is the monoethyl ether of ethylene glycol, with the ether group binding the ethyl group to a carbon atom of the glycol group: $\text{CH}_2 \cdot \text{H}_2\text{C}/\text{O}/\text{C}_2\text{H}_5$.

Another process ¹⁵ starts with ethylene oxide, and causes one molecule of ethyl alcohol to add itself to one molecule of the oxide:



Ethylene oxide, a liquid at room temperature only when under pressure, is pumped into an autoclave into which absolute ethyl alcohol has been added, in the proportions indicated by the reaction and a 15 per cent excess of alcohol. The autoclave is then sealed and the temperature raised to 150°C . (302°F .) and kept there for 12 hours; or it may be heated to 200°C . (392°F .) and kept at that mark for 4 hours. At 150°C ., the pressure rises to 250 pounds per square inch at the beginning of the reaction and at the end falls to 125 pounds. The product is fractionally distilled to remove residual ethylene oxide and alcohol; the glycol ether passes over at about 134°C . (273°F .), leaving in the still the higher-boiling reaction products, such as the ethyl esters of di- and triethylene glycols which are removed to a certain extent. The yield is 70 per cent based on the alcohol used.

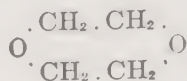
Other Glycol Derivatives. An ether-ester is formed by treating, for example, monoethyl ether of ethylene glycol with acetic acid in the same way; the monoacetate ester of ethylene glycol is prepared. Such chemicals have proved of value as solvents.

The polyglycols and mixed polyglycols are formed by heating the glycol with excess glycols with a moderate amount of phosphoric acid, or other dehydrating agent; they are also obtained as by-products in any reaction in which two glycol molecules might suffer dehydration. Several examples of higher glycols are given in the Table of Relation for ethylene glycol derivatives. The reader will please note that diethylene glycol has one

S. Patent 1,614,883.
S. Patent 1,696,874.

ether oxygen in the molecule, and triethylene glycol two; their properties are therefore rather those of ether-alcohols, and do not closely resemble those of glycerin. Not only ethylene, but also propylene, $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$, butylene, $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$, and their isomers, lead to glycols, one of which gives ethers, esters, and mixed ether-esters and ether-alcohols which may have a special merit in some industrial application. For nitrocellulose and similar lacquer-forming substances, the ethylene glycol derivatives have about the right range of vapor pressure at medium and high temperatures.

Ethylene oxide is formed from ethylene chlorhydrin, by the action of alkali stronger than sodium bicarbonate. Similar cyclic ethers of low molecular weights are now commercial products; thus dioxan, really dioxan:



obtained by distilling ethylene glycol with concentrated phosphoric acid, is of value as solvent.

A modified ammonia has been formed by allowing ethylene chlorhydrin to react with ammonia; triethanolamine is the best known of the three possible modifications. (For properties, see Table 64.) It is of great value as an emulsifier; it forms with fatty acids soaps of unusual properties, and in other ways is finding wide application in the industries.¹⁶ In another method, ethylene oxide is allowed to react with ammonia in an autoclave. The ethanolamines are viscous, hygroscopic liquids of very mild odor; they are organic bases of mild alkalinity, and combine with free fatty acids to form soaps which have solubilities different from those of metallic soaps.

Ethylene diamine is formed by heating ethylene chloride with ammonia under pressure (autoclave). A continuous process has been devised,¹⁷ and in addition, the formation of triamine is essentially prevented by using 15 mols of NH_3 to 1 of $(\text{CH}_2)_2\text{Cl}_2$.



Dichloroethyl ether is formed by the removal of a molecule of water from two molecules of ethylene chlorhydrin.

A new solvent which does not belong among glycol derivatives but which is of synthetic origin has been developed at Purdue University; it is dichlor-2-methyl propane, a liquid. It has excellent solvent properties for grease, and is non-inflammable.

Ethylene reacts with steam at 400° to 500° C. and 25 to 200 atmospheres in pressure, in the presence of a dehydrating catalyst such as thorium phosphoric acid deposited on charcoal,¹⁸ to form ethyl alcohol.

By means of Table 64, some additional information regarding the numerous ethylene and other olefin derivatives is given.

Nitroparaffins. A number of interesting synthetics which are paraffin derivatives made mainly by straight chemical reactions are now available.

¹⁶ See gas purification, Chapter 14.

¹⁷ U. S. Patent 1,832,534.

¹⁸ Brit. Patent 308,859, Jan. 1928.

commercially; they are useful in themselves, as medium-boiling, mild solvents for resins and numerous other substances, and as starting materials for other substances. The new substances are nitroparaffins, nitromethane, nitroethane, 1-nitropropane, 2-nitropropane, nitrohydroxy derivatives, chloronitroparaffins. Hydroxylammonium salts are made from the nitroparaffins.^{18a}

SYNTHETIC METHANOL

The large-scale synthesis of methanol, CH_3OH , the same substance as wood alcohol, from carbon monoxide and hydrogen with the aid of a catalyst substance was brought to the notice of the American public with dramatic suddenness. A few years after the war of 1914-18 (in 1923), with the economic world resuming its normal pace, there were delivered in New York harbor thousands of gallons of synthetic methanol, to be sold, duty paid, at 40 cents a gallon, a price about half that charged for methanol from wood at that time. Readjustments have been made since then, but the advantage remains with the synthetic product. Not only are the raw materials requires cheap and abundant, not only have the technical problems of the medium, and now, high pressure catalysis been solved, but the methanol reaction serves to utilize by-products which otherwise would be wasted; it has been applied to remove an undesirable component of a gas mixture (CO in H_2 for ammonia). For several years, methanol from wood maintained an artificial advantage, because the prohibition law read "wood alcohol, a product from wood," must be used in the chief denaturant formula; in 1929, this advantage was lost. Alcohol from wood must now compete with synthetic methanol for regular commercial and industrial uses.

Since 1923, plants synthesizing methanol have been erected in the United States, and have been most successfully operated. The production in 1939 was 7,766,592 gallons; in 1940, it was 159,271,316 pounds (3 cents a pound); this would be about 24.1 million gallons. For comparison, the production of wood alcohol was 4.8 million gallons, 1939.

When a mixture of carbon monoxide and hydrogen, such as is obtained in water gas, is passed at atmospheric pressure over nickel held at a temperature of 380°C . (716°F .) methane and carbon dioxide are formed: $2\text{CO} + 2\text{H}_2 = \text{CH}_4 + \text{CO}_2$. With the volume adjusted so that to 1 volume of carbon monoxide there are 3 volumes of hydrogen, the reaction goes quantitatively to completion at the temperature of 230° to 250°C . (446° to 482°F .)

With high pressures, and zinc oxide as catalyst, the reaction takes another course; methanol is produced. Since the earliest study¹⁹ of this reaction, improved catalyst, namely, zinc oxide with 10 per cent chromium oxide has been proposed and used. The reaction $\text{CO} + 2\text{H}_2 = \text{CH}_3\text{OH}$ takes place with fewest side-reactions if the ratio of monoxide to hydrogen is 1 to 2.2. The conversion is 20 to 25 per cent, depending not only on repression of side reactions, but also on the activity of the catalyst and on the pressure.

^{18a} A booklet may be obtained from the Commercial Solvents Corporation, 17 East 42nd St., New York.

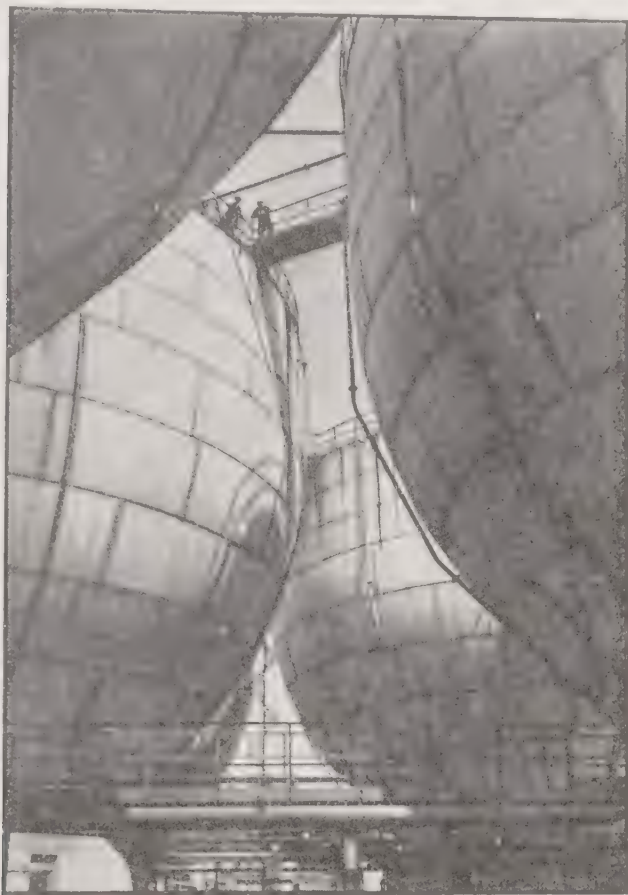
¹⁹ The original catalyst was 90 parts copper oxide with 10 parts zinc oxide, used by Patzsch. For the early history of the methanol developments, see *Ind. Eng. Chem.*, 17, 430 (1925); also Brit. Pat. 229,715 to a Badische Anilin und Soda Fabrik correspondent, reproduced in *Ind. Eng. Chem.*, 17, 430 (1925). See also p. 859, same journal and volume.

²⁰ The Mittasch patent, U. S. Patent 1,558,559.

velocity. For a given catalytic activity, the greater the space velocity, lower the conversion figure.

Since the action $\text{CO} + 2\text{H}_2 = \text{CH}_3\text{OH}$ is exothermic (24 Calories at 25° or 662°F), the amount of methanol in an equilibrium mixture of the gases will be decreased as the temperature is raised; the reaction is aided by relatively low temperatures. Also, as the pressure is increased the amount of methanol rises, for the reaction involves a reduction in moles, from 3 to 1, for the portion of the gases which reacts. At tem-

FIGURE 171.—Storage tanks for synthetic organic chemicals such as methanol, Leuna Works, I. G. Farbenindustrie, Germany. (Bourke-White Photo, Pictures, Inc., N. Y.)



peratures above 250°C . (482°F), less than 0.1 per cent methanol can be obtained,²¹ at atmospheric pressure, while at 300°C . (572°F) and 300 atmospheres, for example, 45 per cent methanol formation is possible. Table 1 gives the percentage of methanol at equilibrium; in commercial practice, the long time required for equilibrium to be attained cannot be provided, and therefore a lower conversion must be accepted.

The catalyst is so chosen that it hastens the reaction, and does not favor the formation of other products. The composition of the catalyst and the method of preparation, as well as the conditions of temperature and pres-

TABLE 65. Percentage methanol at equilibrium ratio $H_2/CO = 2$

Temp. ° C.	Pressure (atm. absolute)					
	1	10	50	100	300	600
200	0.32	28.10	58.40	71.95	85.62	90.70
300	...	0.25	5.47	15.62	43.05	59.80
350	...	0.04	1.02	3.69	19.51	37.11
440	0.20	0.85	6.35	17.30
500	0.07	0.61	2.34
600	0.09	0.37

sure which are found to be most advantageous, must be set. Construction and procedure must take into account the necessity of dissipation of heat from the granules of catalyst, as well as the need of preheating the incoming gases to reaction temperature.

The gas mixture may be 70 per cent hydrogen and 30 per cent carbon monoxide, or 80 per cent hydrogen and 20 per cent carbon monoxide; it may contain small or large volumes of inert gas such as nitrogen, without harm, but in American plants, the nitrogen is either low or absent. The gas mixture of the proper composition is compressed, and the pressure is carried as low as 50 and as high as 1000 atmospheres in different plants. It travels through the converter chamber of suitable material as to structure at a rate which permits a good conversion. Table 66 indicates the conversion which may be expected for various space velocities.

TABLE 66.—Methanol conversion at 400° C. (752° F.).*

Gas mixture	Space velocity	Pressure Atm.	Conversion Per cent
CO + 5H ₂	500	150	22.5
CO + 2.7H ₂	625	204	26
CO + 2H ₂	3000	180	19.5
CO + 2H ₂	7500	180	16.8

* *Ind. Eng. Chem.*, 20, 1111 (1928).

The gas must be free from sulfur, arsenic, and even carbonyls; the latter might introduce iron, and this metal as well as nickel and cobalt must be avoided, for they catalyze the formation of methane.

The converter is preceded by an exchanger in which the outgoing gases give up much of their heat to the incoming ones. After the gas is compressed and heated, it must come in contact only with copper or aluminum surfaces; the converter is of nickel steel, copper-lined. On cooling, the outgoing gas permits liquefaction of the methanol formed; this is removed in a separator, and the unconverted gas is returned to the compressors. The conversion is around 20 per cent. The critical temperature for methanol is 240° C. (464° F.), the critical pressure 78.7 atmospheres; a slight cooling of the converted gas is therefore sufficient to allow liquefaction. Methanol synthesis is exothermic, furnishing enough heat to run the process without outside heat source except when starting.

The methanol synthesis has been employed to rid the hydrogen-nitrogen gas mixture for direct ammonia synthesis from small amounts of carbon monoxide, as already stated in the introduction to this section. In some cases there is present a considerable excess of hydrogen; conversely,

²² In fact, it is recommended in Brit. Patent 306,512 (1928) that an inert gas be added and circulated, in order to dissipate the heat.

centage of carbon monoxide is low. It is necessary to have a highly active catalyst, so that this small amount of carbon monoxide may be completely transformed into methanol. Such a catalyst is obtained²² by melting together pure copper oxide and any oxide of chromium, titanium, molybdenum, zinc, or manganese, breaking up the resulting melt into fragments, and reducing these in hydrogen at 250° to 350° C. (482° to 662° F.). Copper oxide suffers reduction, leaving the metal; the other oxide is reduced. The granules produced by this method are hard, highly porous, and very reactive at relatively low temperatures.

The efficiency of this catalyst is high, which means that the percentage of ethanol (as gas) in the gas mixture leaving the reaction bomb is high for each unit volume of catalyst, at given pressure and temperature, compared with other masses. The metallic copper tends to dissipate the heat of reaction and thus favors formation of methanol.

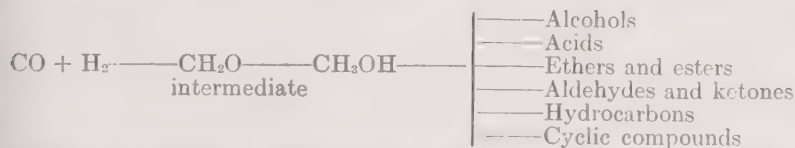
The catalyst so produced will cause as little as 3 per cent carbon monoxide in the hydrogen gas to react. Pressures of 200 to 300 atmospheres are suitable, but at 1000 atmospheres the reaction proceeds smoothly.

The methanol formed is removed by cooling the compressed gas to between 0° and 20° C. (32° and 68° F.), when it liquefies; the residual gases are returned to the high-pressure system and sent to the ammonia converters. Carbon monoxide is avoided in the methanol converters, because it may allow a deposit of metallic zinc to form, which the gas would carry to the iron catalyst, poisoning it.

In all catalytic processes, the preparation of the catalyst is an important operation. For the methanol catalyst, the following preparation²⁴ will serve as an example: Zinc oxide is stirred into a chromium nitrate solution, and the whole evaporated to dryness; the heating is continued until the nitrate is converted into oxide. The product is mixed with dextrin solution containing zinc chloride, then dried and granulated. The catalyst is used in the converter in granule form.

In distilling the synthetic methanol it is found to contain a higher-boiling fraction, consisting of higher alcohols. An explanation for their formation from methanol has been offered.²⁵

The term "methanol synthesis" has come to stand for a series of syntheses in which the oxides of carbon and hydrogen. The six main classes of compounds which are obtained are shown below:



The reaction achieved depends upon or is governed by the nature of the catalyst; with zinc oxide, as has been shown, the main reaction, the production of methanol, is favored, and the side reactions are repressed. By the use of cobalt metal with chromium oxide, for example, the formation of

²² U. S. Patents 1,844,857 and 1,844,129.

²⁴ Brit. Patent 272,864 (1926).

²⁵ Higher alcohols formed from carbon monoxide and hydrogen, by G. D. Graves, *Ind. Eng. Chem.*, 44, 171 (1931).

hydrocarbons is favored. The desired side-reaction is produced and the exclusion of all the others by the proper choice of catalyst, and especially by the use of mixed catalysts.

Methanol is an antifreeze for automobiles, a solvent for lacquer manufacturers, the raw material for most of the formaldehyde made, for methyl chloride, and to a minor degree, a denaturant for tax-free alcohol.

The total of non-coal tar synthetic organic chemicals produced in the United States in 1940 was 1,989,284,000 pounds valued at \$265,307,000.

GENERAL STATEMENT REGARDING THE CHOICE OF CATALYST

Many of the reactions discussed in this chapter are catalytic in nature. Elsewhere in the book a number of others will be found in their proper place. Some of these are indicated in Table 67, "Some Catalytic Reactions of Industrial Importance." A few general remarks regarding catalysts and their function will supplement the information given elsewhere, and clarify some of the underlying general principles.

The original discoveries, by Sabatier, consisted mainly of hydrogenation of hydrocarbons in the vapor phase, in contact with metallic nickel especially at ordinary pressures. Today, nickel and other metals of the same type, cobalt, iron, copper and platinum, are still used for hydrogenation, for example, that of vegetable oils for the production of edible and non-edible vegetable fats.

There are two ways in which a catalyst may lose its efficiency: one by heat, the second by poisoning. Nickel is sensitive to impurities, so much so that the hydrogen used must be absolutely pure, and the material to be hydrogenated must not contain any elements which might affect the nickel. The same applies to the other four metals listed.

In the hydrogenation of mineral oil, in hydrofining, it is out of the question to use such a delicate material as nickel, or any metal sensitive to sulfur. Fortunately, a number of oxides have been found to have excellent hydrogenating functions, and at the same time are resistant to impurities, and, properly chosen, also to the deactivating effect of continued heat. Such hydrogenating oxides are molybdenum, tungsten, manganese, vanadium and chromium oxides, with alumina, magnesia, zinc oxide, and potassium carbonate as promoting agents (used in small amounts).

For hydration and dehydration in the vapor phase, the oxides which are most efficient and durable are thoria, alumina, tungstic oxide, silica, titania and zirconia; also those of the alkalies and alkaline earths.

The hydration of acetylene takes place in the liquid phase, and the most satisfactory material is mercurous sulfate.

For oxidation processes the metals of the platinum series, as well as their oxides and salts of metals which can exist in two or more states of oxidation, are the most important catalysts.

GENERAL REMARKS ON CATALYSIS ^{25a}

A distinction is made between atmospheric, or low-pressure, catalysis and high-pressure catalysis. As one would expect, the first work of Sabatier

^{25a} See "Catalysis, Inorganic and Organic," by Berkman, Morrell, and Egloff, New York, Reinhold Publishing Corp., 1940.

was at low pressures, and only subsequently was the field of high-pressure catalysis developed. Differently constructed equipment had to be devised of materials able to withstand high pressures and elevated temperatures and the accelerated chemical activities on container walls. A vast amount of information on the compressibility of gases and gas mixtures, on the flow of compressed gases through narrow bores, and on chemical equilibrium had to be obtained, before the present state of development was reached. The application of catalytic reactions to industrial processes has only been possible.

It was formerly held that a catalytic agent accelerated a reaction which was slow, but could take place of itself. It is well to modify this in several respects, and to say: A catalyst hastens a slow, or even very slow chemical change, which, however, must be thermodynamically possible, and, with several products are obtainable, the catalyst is capable of directing the reaction.

Any substance which accelerates a reaction is a catalyst; it may be a substance dissolved in a liquid in which gases must in their turn dissolve, such as the violet acid in the sulfuric acid-nitric oxide chambers, or hydrogen chloride and tin compounds in some of the hydrogenations of tars and coal to give motor fuels. The contact catalyst is frequently a solid which is exposed to the gases, vapors, or to the liquid in which the reaction is to take place; the solid may be in lump form, or powder; it may be itself, or it may be supported on a "carrier," which is inert.

In the language of chemical kinetics, the catalyst works to overcome the energy of activation, which must be furnished to the molecule before it can react. The catalyst does not displace the equilibrium; it raises the rate of the reaction at which the equilibrium is attained, or approached.



FIGURE 172.—The surface of metallic nickel, greatly enlarged to show the catalytically active centers formed by protruding atoms. (After Taylor.)

The activity of, let us say, a metal surface in the case of hydrogenation is due to the surface of the metal. A comparatively small number of surface atoms project into space, and are unbalanced with respect to their chemical affinities or valence. (See Fig. 172.) These projecting atoms form intermediate compounds, or complexes with the hydrogen; the forces involved are not distinguishable from the common chemical forces. If one active center, or a near-by one, can also attract the second reactant, such as carbon monoxide, similarly distorting its normal structure, the two substances can meet while in the active state, and readily form a new grouping. Questions of adsorption are of the first importance; in some cases adsorption stops the process. For example, 3 per cent carbon monoxide in hydrogen will retard ammonia formation, because the monoxide is adsorbed by the surface, thus preventing the approach of the hydrogen. The monoxide is then spoken of as a poison. Promoters in this

be substances which distort the crystal lattice in the catalyst still more than it normally is; in other cases, these promoters would be able to break the temporary complexes with the reactants which are necessary for rapid change.

The rôle of temperature will be a compromise between two or more effects; it must not be so high that the adsorbed atoms and molecules are driven off so fast that no or little reaction can take place; yet it must be high enough so that the activation of the reactant molecules is a maximum, and a very little additional force at the contact surface will suffice to form the reaction complex.²⁶

The events in the catalyst case may be affected by other factors than the rate of reaction or the activity of the catalyst; for example, by rates of diffusion, as presented in the first chapter.

A figure in constant use in catalytic reaction studies is the space-velocity, by which is meant the volume of reacting gases passing over one unit of catalytic mass per hour. The volume in question is the volume of exit gases, calculated to normal conditions of temperature and pressure, while the volume of catalytic mass is the volume occupied by the mass spread out or packed in the reaction vessel.

The greater number of catalytic reactions presented in these chapters are heterogeneous, that is, involve two or more phases, such as solid and gas, solid, liquid and gas. A homogeneous catalytic reaction would be the reaction of sucrose in solution by a dissolved acid. A heterogeneous catalytic reaction involving three phases is the hydrogenation of edible oil in which hydrogen (gas), the oil (liquid) and the contact substance, nickel (solid), participate.

HYDROGENATION AND OXIDATION OF HYDROCARBONS

Among the most important catalytic reactions are those which incorporate into a hydrocarbon from natural sources, such as naphthalene or benzene, hydrogen or oxygen. The solid naphthalene, on gaining 4 hydrogen molecules, turns into the liquid tetralin; on oxidation, the liquid benzene turns into the solid maleic acid. A great variety of products have been obtained, and they might indeed, as suggested in the introduction to this chapter, be called semi-synthetics. It is, however, customary not to make the distinction, but to speak of them as synthetics.

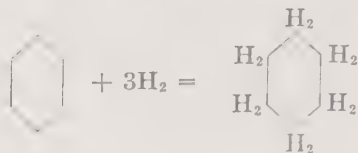
Tetralin. Naphthalene vapors mixed with hydrogen (very pure) are passed over nickel held at 150° to 200° C. (302° to 392° F.), at ordinary pressure; tetralin is formed: $C_{10}H_8 + 2H_2 = C_{10}H_{12}$. Naphthalene melts at 80° C. (424.4°); tetralin boils at 205° to 207° C. (401° to 405° F.). This is the hydrogenation in the vapor phase.

Naphthalene may be melted in an autoclave with stirrer and nickel suspended in it, very much as is done for the hydrogenation of edible oils; at 140° to 160° C. (284° to 320° F.) hydrogen is forced in under a pressure of 30 atmospheres. Tetralin is formed. On long-continued hydrogenation, decalin is obtained, largely: $C_{10}H_8 + 5H_2 = C_{10}H_{18}$. The latter

²⁶For the theory of the mechanism of catalytic processes, see "Eighth report of the committee on catalysis," J. C. W. Frazer, *J. Phys. Chem.*, **34**, 2155 (1930).

substance is more expensive to prepare, and has no great advantage tetralin, so that its industrial importance is small.

Benzene vapors with hydrogen over nickel at 140°C . (284°F .) cyclohexane, $\text{C}_6\text{H}_6 + 3\text{H}_2 = \text{C}_6\text{H}_{12}$, a liquid. Expressed graphically:



Phenol by a similar procedure gives cyclohexanol.

Phthalic Anhydride. By controlling the oxidation by air of naphthalene a good yield of phthalic anhydride may be obtained; the catalyst vanadium pentoxide, at an elevated temperature. This was one of the earliest triumphs of catalytic chemistry outside of sulfuric acid synthesis. By controlling is meant arresting it at a certain stage, for should it be allowed to proceed unchecked, only carbon dioxide and water would be the products.

In the most successful of the commercial installations,²⁷ air and naphthalene vapors from boiling naphthalene are thoroughly mixed in a heating chamber, and passed over the catalyst in numerous square tubes, at about 357°C . (674.6°F .), in a downward direction. Figure 173

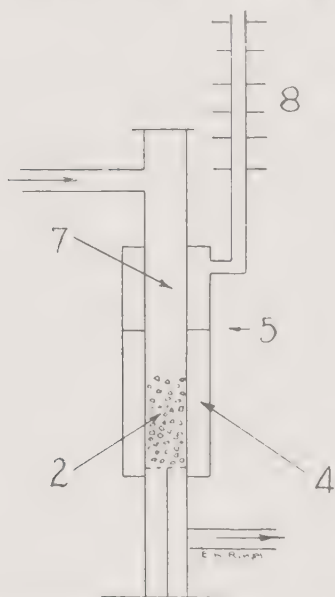
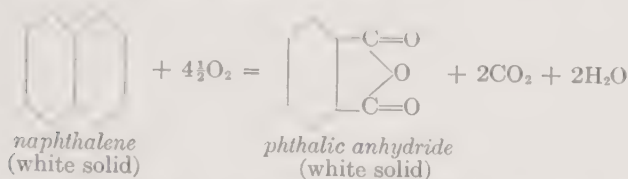


FIGURE 173.—Air-hydrocarbon oxidation. Single tube, with catalyst mass 2; level of mercury in the jacket 5; total condenser for the mercury 8; preheating part of reaction tube 7. In the full size installation, a nest of tubes is used.

illustrate the disposition. Around the tubes a small body of liquid mercury is gently boiling. The converter consists of a nest of such tubes submerged in mercury, the whole surrounded by an outside jacket; the latter carries a vertical tube with fins which acts as an efficient condenser for the mercury. As the hydrocarbon and air react (on the surface of the vanadium

²⁷ U. S. Patent 1,374,720; for the basic patent of Gibbs, see U. S. Patent 1,285,117. See also U. S. Patent 1,444,068. In 1930, the Gibbs patent was cancelled, and U. S. Patent 1,787,417 and 1,787,418 issued to Alfred Wohl, for the same process. These were attacked in court by the government. In 1934, the Wohl patents were upheld and declared valid (see Chapter 40).

side), much heat is evolved; it passes through the wall of the square to the mercury, which consumes it by vaporizing. In that way, the temperature is maintained near the boiling point of mercury, 357° C (673° F.). The upper half of the catalyst tube is empty, and this part serves the preheater for the incoming gases, which are already at an elevated temperature. The main reaction is:



to a certain extent, benzoic acid, $\text{C}_6\text{H}_5\cdot\text{COOH}$, and naphthaquinone,

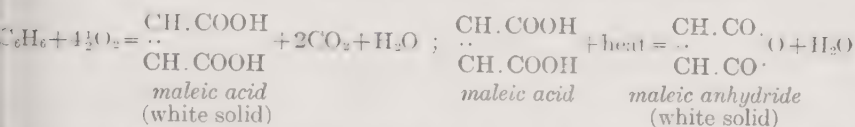
$\text{C}_{10}\text{H}_6\text{O}_2$ are formed, and are collected with the anhydride, while the

pass out. A 72 per cent recovery of phthalic anhydride is feasible; it is obtained by sublimation, and is put on the market in the form of flakes and crystals.

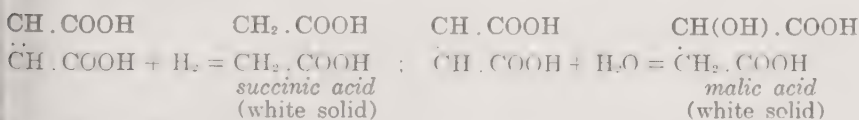
In the original installations, the catalyst was made by dipping asbestos into ammonium vanadate, and activated by passing hot air through it. Instead of asbestos, pumice may be used. The square tubes are used as catalyst carriers because the ratio of surface to content is greater for a square than for a round one of same height and same cubical content. It should be noted that this oxidation is performed at atmospheric pressure. The temperature may be varied by operating under slightly higher pressure. Instead of mercury, liquid sulfur may be used.²⁸

The production of phthalic anhydride by catalytic oxidation in the United States was 57,946,415 pounds in 1940, valued at 14 cents a pound.

Maleic Acid. In the same apparatus serving for phthalic anhydride production, maleic acid is formed by the oxidation of benzene at a slightly higher temperature. A recovery of 60 per cent is considered good.



Maleic acid may be hydrogenated to succinic acid, or hydrated to malic acid; the latter is a substitute for citric acid in beverages. The esters derived from these acids in the standard way are valuable for their odor and solvent properties.



The United States production of maleic anhydride in 1940 was 4,497 pounds, valued at 25 cents a pound.

Purification by Catalysis. The best available anthracene of commerce contains 30 to 50 per cent anthracene, $C_{14}H_{10}$; the chief impurities are carbazol, $C_{12}H_9N$, and phenanthrene, $C_{14}H_{10}$. It has been found possible to effect a purification by catalysis. The crude material is mixed in vapor form with air (1 to 35) by spraying the melted crude into hot air (1000 F.). The mixed gases are passed over a properly chosen catalyst at $350^{\circ}C.$ (1000 F.). The carbazol is destroyed, while practically all the anthracene and phenanthrene are recovered unchanged. The phenanthrene may now be isolated by the use of a solvent, leaving a 90 to 99 per cent anthracene. A catalyst which favors the total combustion of carbazol and at the same time leaves the anthracene unaffected is made by suspending titanium dioxide (TiO_2) in a water solution containing 12 parts of potassium hydroxide, cyanide or nitrate, either singly or mixed; this suspension is coated on pumice broken to pea size, and dried. A number of other formulas are available.²⁹ A high grade anthracene is also obtained by dissolving crude anthracene in furfural and crystallizing.²⁹ Related reactions are shown in Table 68.

TABLE 68.—*Hydrogenation and oxidation of natural organic compounds.*

Compound	Catalyst	Temp. ° C.	Pressure Atm.	Product
Naphthalene + $2H_2$	Ni	150–200	1	tetralin
Benzene + $3H_2$	Ni	150–160	1	cyclohexane
Phenol + $3H_2$	Ni		1	cyclohexanol
Benzene + $4\frac{1}{2}O_2$	V_2O_5	400–440	1	maleic acid
Naphthalene + $4\frac{1}{2}O_2$	V_2O_5	350–400	1	phthalic anhydride
Toluene + $1\frac{1}{2}O_2$	MoO_3 ; UO_2	400	1	benzoic acid
Anthracene + $1\frac{1}{2}O_2$	V_2O_5	400	1	anthraquinone

OTHER PATENTS

U. S. Patent 1,598,560, on the absorption of ethylene in sulfuric acid, then water to form ethyl alcohol; 1,599,119, ethylene and sulfuric acid to make n-butyl sulfate; 1,574,796, on ethyl sulfuric acid and ethyl sulfate from ethylene and sulfuric acid, catalyzed by ferrous or cuprous salts; 1,460,545, production of ethyl alcohol from ethane in natural gas; 1,402,336, production of ethylene from ethyl alcohol; 1,779,710, ethylene glycol ester of abietic acid; 1,569,775, on the absence of effect of iron in methanol synthesis, and a chromium oxide-manganese oxide catalyst; 1,710,000, on methanol synthesis; 1,824,896, on formaldehyde formation followed at once by hydrogenation with the aid of a second catalyst; 1,861,841, on dehydrating acetic acid with carbon tetrachloride; 1,875,273, production of methyl alcohol by passing gaseous mixture of hydrogen and carbon monoxide in contact with a catalyst mass comprising 50 per cent by weight of reduced copper, 300° to $400^{\circ}C.$ at 5 to 300 atmospheres pressure; 1,961,736-7, forming acetic acid from methane and carbon monoxide, J. C. Carlin and N. W. Krase; 2,031,475, oxidizing catalyst, J. C. W. Frazer; 2,040,233, preparing contact catalysts; 1,925,602, on a stabilized catalyst for metal degreasing; and 1,907,875, on an apparatus for that purpose.

PROBLEMS

1. The manufacture of ethylene glycol consists of treating ethylene chloride with a solution of sodium bicarbonate. The chemical equation is given in the text. The chlorhydrin is made by the action of ethylene on hypochlorous acid. The hypochlorous acid is liberated at the moment it is to react by the action of chlorine on a solution of sodium hypochlorite. This substance in turn is made by the action of chlorine on a cold solution of caustic soda.

The chemical reactions are given in the text.

²⁹ *Ind. Eng. Chem.*, 20, 1330 (1928).

Assuming the yields to be 100 per cent, find how much chlorhydrin was required to make 1 ton of ethylene glycol; and how much hypochlorous acid and ethylene to make the required ethylene chlorhydrin; how much sodium hypochlorite to obtain the necessary hypochlorous acid; how much chlorine to produce the sodium hypochlorite, and which second amount to liberate the free hypochlorous acid.

Let the reaction for the formation of the glycol from the chlorhydrin be realized to the extent of 90 per cent, and the one for the formation of chlorhydrin from methylene and hypochlorous acid also to the extent of 90 per cent; what will be the amount of each of the items listed in (a)?

Express the required amount of ethylene in cubic feet at 62° F. and 1 atmosphere's pressure; the weight for one cubic foot is 0.0738 pound.

The formula for the heat of reaction for the formation of methanol in gas from carbon monoxide and hydrogen is

$$\Delta H = -18.050 - 19.54T + .01586T^2.$$

plies to any temperature; the heat value is found by substituting for T the temperature of reaction in absolute degrees (or degrees Kelvin). This expression is derived from the free energy expression

$$\Delta F = -18.050 + 45.00T \cdot \log_{10} T - .01586T^2 - 69.4T.$$

change in free energy for a reaction is of more importance and influence than heat effect.

The exact value for the heat of reaction in the table is $\Delta H_{298} = -24.050$ gram-calories or -24.059 Calories. Check this value, and find the heat effect for 400° C., C., and 325° C. Compare the results. In every case, it is for how many grams methanol?

The reaction for making methanol is $2H_2 + CO = CH_3OH$. In order to make gallons of methanol 100 per cent pure, how much hydrogen by weight will be required; how much by volume at 0° C. and 1 atm.? The reaction is made to take place at 300° C. and 1000 atm., so that the gases entering the catalytic chamber are under that pressure and raised to that temperature. What will be the volume of entering gases which actually do react?

If the conversion is 25 per cent; what is the weight and volume of the gases into the converter?

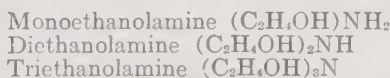
If the catalytic volume is 10 liters; with the outgoing methanol assumed to remain pure, and the 100 gallons to be obtained in a period of 10 hours, what is the reaction velocity?

Calculate the volume of the compressed gases in two ways, first, according to the ideal laws; second, with the use of the compressibility coefficients:

Temp. ° C.	Pressure Atm.	Hydrogen	Carbon monoxide	Methanol
0	1	1	1	1
300	1000	2.8157	3.3203	3.3

Compare problems in Chapter 6.)

Chlorhydrin, $OH \cdot CH_2 \cdot CH_2 \cdot Cl$, reacts with ammonia, NH_3 , to form three products,



These in turn are capable of reacting with acids such as stearic acid, $C_{17}H_{33}COOH$, to form soaps which are excellent emulsifying agents.

1) Assuming commercial triethanolamine to contain 17.5 per cent DEA, and 5.0 per cent MEA, what is the theoretical yield from 1000 lbs. of chlorhydrin?

2) What is the combining weight of the commercial TEA?

3) What weight of NH_3 is required for making the TEA, in (2)?

4) What weight of stearic acid will combine with the commercial TEA, formed?

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Through his activity in synthesizing dyestuffs, the chemist has become interested in dye application: the science of using the proper dye, whether artificial or natural, for a given fiber.

Chapter 26

Dye Application*

In the application of dyes, two main factors have to be observed: the character of the fiber, and the properties of the dyestuff.

The character of the fiber: Cotton consists of pure cellulose: it has very few properties, either acid or basic. Silk and wool in contrast to cotton have pronounced acid and basic properties. Consequently dyestuffs with pronounced acid or basic properties can be applied directly to wool and silk; to cotton only special classes of dyes, among others the benzidine dyes, are direct dyes, and are used in the form of the sodium salt. In addition, coloring matter may be fastened onto cotton in a roundabout way, by means of an intermediate compound, as in mordanting, or by building the color in stages on the fiber.

The properties of the dyestuffs, whether acid or basic, soluble or insoluble, acidifiable or not, must be considered in their application; various classes of dyes require different methods.

THE CHARACTER OF THE FIBER

Cotton. Cold concentrated sulfuric acid dissolves cotton, and on diluting with water, dextrin is precipitated. Warm dilute sulfuric acid forms hydrocellulose (hydrated cellulose) and the fibers swell; in the cold, diluted mineral acids have no action. Organic acids at room temperature have no action; at higher temperatures, the strength of the fiber is weakened. Diluted caustic, or milk of lime boiled with cotton without access of air, has no action, but in presence of air, oxycellulose is formed. Concentrated alkali causes the cotton filament to swell and the walls of the fiber to become cylindrical, resembling tiny glass rods. If the caustic treatment is performed while the cotton is under tension, so that the fiber cannot shrink lengthwise, the cotton develops a silk-like luster. This process is called mercerization. The affinity of the mercerized thread for dyes is much greater than that of untreated cotton, because of the oxycellulose which has been formed.

Silk. Cotton consists of a single substance, cellulose, whereas silk consists of two: the fibrous substance, fibroin, and the silk gum, sericin. The sericin covers the fiber; it is soluble in water and soap and can be rapidly removed by boiling, while the fibroin is insoluble. The silk threads of commerce are fibroin; and it is to this part of the original substance that the following remarks apply.

Concentrated mineral acids destroy silk; diluted acids are readily absorbed by silk; wool is acted on in the same way. Hot caustic soda will dissolve silk completely, but not so fast as wool.

*In collaboration with Robert Kuoch, Ph.D. (Basel), Consulting Chemist for Dyes, of Buffalo.

Tin, aluminum, and iron salts are adsorbed by silk as well as by wool with the formation of a metallic hydrate or an insoluble basic salt.

Affinity of silk for coloring matters is in general lower than that of wool; for instance, acid colors on silk are not as fast to washing as when applied to wool.

Wool. Diluted mineral acid does not affect wool, except that the color is retained by the fiber with great tenacity; it cannot be removed by boiling with water. This is well shown as follows: Wool which has been treated with dilute sulfuric acid and then washed with boiling water several times until the water shows a neutral reaction may be dyed in a new bath with a dye which ordinarily is applied in an acid bath.

Wool is readily attacked by alkali; the higher the temperature, the more effective the attack.

This fiber behaves toward dye in different ways according to its origin, so that it is essential to obtain the wool from the same source, or be careful to make preliminary dyeings; but in all cases its affinity for dye is greater than that of silk, as was stated previously. It will be remembered, too, that both wool and silk have a far greater affinity for dye than has cotton. Wool has pronounced acid and basic properties; it may be considered an amphoteric acid. It is classed as a protein substance.

Aluminum sulfate, ferrous sulfate, chrome alum, and other salts having acid properties are readily adsorbed by wool; neutral salts are not adsorbed. The application of salts to wool is called mordanting; although important, it is less so than the mordanting of cotton.

Rayon. In this synthetic fiber, a distinction must be made between viscose silk, or rayon, and cupranmonium rayon, on the one hand, and acetate rayon, on the other. The first two are essentially cellulose, and behave like cotton; they may be dyed in the main by means of the common dyes. Acetate rayon is cellulose acetate, and has different properties; its affinity for dyes is distinct from the affinity cotton shows. Special dyes have been developed, among others, those which are colloiddally dispersed amidoazo intermediates. The material is adsorbed by the fiber and is developed as described under Developed Dyes. Acetate rayon is attacked by caustic soda, a hydroxyl group replacing the acetyl group. This may be turned to advantage by allowing only a slight attack and then applying dyestuffs which would not be received were the hydroxyl group absent.

Nylon. This distinctly new material, already described in Chapter 1, is in one of its varieties, a superpolymer (molecular weight above 10,000) of hexamethylene diamine and adipic acid. Made into a fiber, it is the truly synthetic fiber, and has a closer similarity in both constitutional and physical properties to natural silk than has any other. Nylon fiber has the appearance and luster of silk; the degree of luster can be modified as desired by the use of a delusterant. Its tensile strength is higher than that of silk, rayon, or cotton. The best dyes for nylon are the so-called acid colors, although by introducing modifications it may be possible to use other dyes.

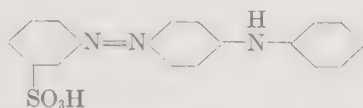
¹ *Chemical News*, 128, 19 (1924), also a number of articles in volumes 14 and 15, of the *Dyestuff Reporter*.

iberglas. Glass fibers already briefly discussed in Chapter 11, are being produced in a number of shades, including tans and browns. These could not be dyed in the usual sense, but they need not be, for they are colored in the glass batch. Special methods are used to spin the fibers, and weaving is done in the usual manner. The glass fabric is fireproof and of value for scenic drops, stage curtains, and tablecloths. Another use which depends upon the inertness of the fabric is in the form of filter for the filtration of high concentration acids and alkalis, a plant application of the laboratory filter medium, glass wool. The fabric is also used for ladies hats and wearing apparel.*

THE PROPERTIES OF DYESTUFFS

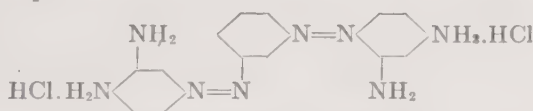
Dyestuffs are chemical compounds which have the property when in solution to color animal or vegetable fibers permanently, with or without the use of auxiliary agents. They may be divided into natural² and synthetic dyestuffs, with the latter class now the more important; but the colorist divides all dyestuffs rather on the basis of whether or not preliminary treatment is necessary in applying the dye to the fiber. From this point of view, dyestuffs may be divided into, *a*, direct dyes for cotton, *b*, direct dyes for wool and silk, and *c*, indirect dyes (developed dyes). This system of classification will be used in the following discussion, but first the meaning of the terms *acid dyes* and *basic dyes* will be made clear, because these expressions are in constant use.

Acid dyes are dyes which have a pronounced acid character; they are usually sulfonic salts of azo bodies, or sulfonic derivatives of basic dyes; acid dyes do not include the direct dyes for cotton, such as the benzidine dyes, even when these contain an acid group.



*Metanil Yellow, an acid dye*³

Basic dyes are hydrochlorides, sulfates or oxalates of organic bases; by the latter is meant a substance containing besides a benzene or other aromatic nucleus, an amino group or certain other groups containing nitrogen. Thus Bismarck Brown is the hydrochloride of a basic azo dye containing four amino groups:



Bismarck Brown, a basic dye

Other basic dyes are Malachite Green, which is a triphenylmethane dye, and Methylene Blue, a thiazine.

²Fiberglas, decorative yarns and fabrics." *American Dyestuff Reporter*, 30, No. 5, p. 115.
³Areas of cultivation and production figures for natural dyestuffs will be found on p. 54 of *Putnam's Economic Atlas*, London, George Philip and Son, Ltd., and New York, G. P. Putnam's Sons, 1925.
 The hexagon stands for benzene, C₆H₆; when a group (thus -SO₃H) is attached to the ring, it is understood that the hydrogen at that place is missing.

Direct Dyes for Cotton. Direct dyes for cotton are sodium salts of the benzidines, primulines, and a few others which contain the sulfonate (SO_3H) or carboxyl (COOH) group; such sodium salts have direct action on cotton, but the corresponding free acid dye has not. They are applied in a neutral or slightly alkaline solution. Examples: Congo Red, Brilliant Yellow.

Direct Dyes for Wool and Silk. Acid dyes are direct dyes for wool and silk; they are manufactured and shipped to the textile mill in the form of the sodium salts of such dyes, but the dye bath is made acid by the addition of sulfuric or acetic acid, so that the free dye is formed, that is, so that the sulfonic or carboxyl groups are free; in that state the dye is readily adsorbed by the animal fiber.

The basic dyes are direct dyes for wool and silk.

Indirect Dyes. The basic dyes are indirect dyes for cotton. The latter must first be treated with tannin; as tannin is the mordant, the use of basic dyes entitles them to a place among the mordant dyes. As regards the latter, the tannin dyes are relatively unimportant.

Mordant Dyes. These comprise, in addition to the above, those which require preliminary treatment of the cotton with a metallic salt solution, followed by immersion in an ammonia solution, before the dye is applied. The ammonia treatment precipitates insoluble metallic hydroxide on the fiber and in the fiber; to this hydroxide, the dye becomes fixed on turn. These insoluble, stable, colored compounds of metal and dye are termed "lakes." Alizarine, originally a natural dyestuff, now made together synthetically, is an example; it gives different colors with different salts, red with aluminum or tin, red-brown with calcium, blue-black with iron, and brown with chromium salts. A total of over 200 dyes, derived from alizarine or closely allied to it, forms the class called alizarine dyes. The original alizarine, which is also the simplest, is still widely used. Its formula is given in the next chapter.

Chrome Dyes. A direct dye is first applied to wool, the only fiber which is chrome-dyed, in an acid bath; the wool is then given a treatment with a solution of sodium dichromate, resulting in the formation of a chrome lake on the fiber. Example: Diamond black.

Sulfur Dyes. Sulfur dyes are cotton dyes; they must be reduced to a solution of sodium sulfide (Na_2S), forming a soluble compound called leuco⁴ compound, which is adsorbed by the cotton. The dye is then oxidized (called development) in the air, and the insoluble sulfur dye is thus re-formed on the fiber itself. Such a process of re-forming the dye from its soluble leuco compound makes it extremely fast. Examples: Sulfur Black, Sulfur Blue.

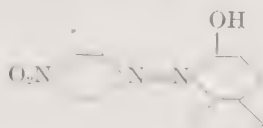
Vat Dyes. Vat dyes are also cotton dyes; and like sulfur dyes, they are insoluble in water. They are reduced with sodium hyposulfite⁵ ($\text{Na}_2\text{S}_2\text{O}_4$) with formation of the soluble, colorless or slightly yellow leuco compound which are readily adsorbed by cotton. By exposing the treated cotton to air, the dye is re-formed on the fiber.

⁴ The term leuco compound is applied solely to the soluble reduced body formed from the dye by reduction.

⁵ The correct chemical name is sodium hyposulfite. It is erroneously called sodium tetrathiosulfate in the trade.

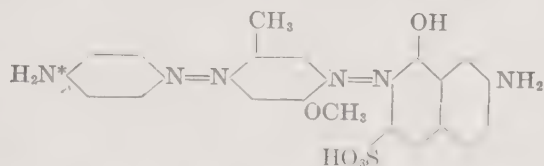
the original insoluble dyestuff reappears, fixed to the fiber so that it can be washed out. Examples are Indigo and Indanthrene; both are indanthrene extremely so. The formula of both of these substances is in Chapter 28.

Developed Dyes. The developed dyes are insoluble. They are manufactured in stages, directly on the fiber. In the case of Para Red for example, the cotton fiber is treated with β -naphthol dissolved in caustic, then passed through a diazotized paranitraniline solution; the formation of Para Red takes place on the fiber.



Para Red

Another group of developed dyes involves dyeing by means of a direct dye followed by diazotization on the fiber, and this in turn by coupling, so that another intermediate enters the molecule; it is a combination of direct dyeing and developed dyeing. These operations render the dye faster, that is, more resistant to washing and light. For example, Zambesi Black Dye involves the following operations: The direct dye whose molecule has the following position



PROCESS OF DIRECT DYEING WITH ACID DYES

Silk. Silk is placed in a bath containing the acid dye dissolved in the form of its sodium salt together with soap; enough dilute sulfuric or acetic acid is added to make the bath weakly acid. The dye bath is cold or lukewarm.

The dyes which may be used are, among many others: Ponceau, Congo Red, Scarlet, Eosine, Acid Fuchsin, Rhodamine, Rose-induline, Crocein Orange, Azoflavine, Methyl Yellow, Tartrazine, Patent Green, Alkali Blue, Prussian Blue, Induline, Resorcin Brown, Naphthol Blue Black, Naphthol Black.

Wool. The dye bath is charged with the necessary amount of acid dye which dissolves, again in the form of a solution of the sodium salt; 2 to 5 per cent sulfuric or acetic acid is added in sufficient amount to liberate the free dye. The temperature is raised to 40°-50° C. and the wool introduced. Ten to 30 per cent Glauber salt, ($\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$), based on the weight of the wool, is added and the bath slowly heated to boiling by direct steam. The dye leaves the bath and attaches itself to the fiber. If the dyeing goes on too fast, the cloth is blotchy; this may be prevented by adding aluminum sulfate or acid sodium sulfate instead of sulfuric acid.

A slight modification of the method consists in dissolving the sodium salt of the dye for the bath, introducing the wool, and then adding the dye very slowly, in small portions.

The dyes which among others may be used for wool are the same as those listed under direct dyeing of silk with acid dyes.

Cotton. Before dyeing, cotton should be placed in a soap solution for an hour; it may then be introduced into the dye bath containing 2 to 5 per cent of dye for each 100 pounds of cotton, either as yarn in skeins, or as cloth. This is expressed as 2 to 5 per cent. One of the following salts is added to the dye bath: Glauber salt, common salt, borax, sodium phosphate, ammonium carbonate. The bath is then brought to a boil and maintained there for some time, until the bath is exhausted of dye. The function of the salt added is to diminish the solubility of the dye, and thereby hasten the exhaustion of the bath. The cotton is next washed and dried.

The dyes that are suitable are members of the stilbene, benzidine, and primuline groups, such as Sun Yellow, Brilliant Yellow, Primuline Yellow, Congo Red, Direct Sky Blue, Direct Green B, Bordeaux, Scarlet and others. Every shade is represented in these direct cotton dyes.

Many dyestuffs are precipitated by calcium and magnesium salts, so that a bath made up with ordinary ground water would result in precipitation of the dye; this is the reason why soft water must be used in the dyeing.

MORDANTING WITH TANNIN

Mordanting with tannin concerns cotton chiefly. The cotton is placed in a hot water solution of tannin, and then in a lukewarm solution of the dye, for instance. Antimony tannate is now fastened to the fiber, and is insoluble. The goods are next passed slowly through a solution of the dye.

The basic dyes listed in the following division are suitable for cotton mordanted with tannin.

If the cotton is treated with sulfonated castor oil before mordanting, the dyeing is more even, and the fiber is more pliant (softer). This is true of all cotton dyeing. The concentration of the oil is 10 grams per liter.

PROCESS OF DIRECT DYEING WITH BASIC DYES ON WOOL AND SILK

For wool and silk, no tannin is needed, for they already contain an acid group in the molecule. The basic dye is dissolved in water, the temperature raised to 50° C., and the wool or silk is introduced. The temperature is raised further gradually, over a period of half an hour to the boiling point, when the process is completed. The material is washed with water and dried. Examples of basic dyes are: Fuchsine, Rhodamine, Safranine, Auramine, Phosphine, Malachite Green, Methylene Blue, Rosaniline, Mauve, Methyl Violet, Bismarck Brown. The first synthetic dye was a basic dye, mauve.

METALLIC MORDANTS

The procedure differs somewhat for the several fibers; the application to cotton is the most important. Cotton is treated with a solution of the metallic salt, such as aluminum sulfate. Next it is passed into an ammoniacal bath, and after that, into a solution of alizarine in ammonia water; sometimes the last two baths are combined. Wool and silk can dissociate in metallic salts, so that when they are placed in the salt solution, and heated, the basic part of the dissociated salt deposits on the wool or silk. The rate of deposition is controlled by adding more or less potassium acid sulfate, which retards it. After that, the wool or silk is placed in the alizarine bath.

Examples of dyes applied with metallic mordants: Synthetic dyes—Alizarine, Alizarine Maroon, Purpurin, Anthrapurpurin, Anthracene Blue. Natural dyestuffs—Logwood, for blue and black, Cochineal, for red, Quercetin, for yellow.

In order to form lakes, hence to be adaptable to this kind of dyeing, the molecule of the dye must contain two hydroxyl groups in the ortho position to each other, or one hydroxyl group with one of the following groups in the ortho position: carboxyl, COOH, nitroso, NO, azo, N = N, imide, NH.

The process for vat dyes, developed dyes, and sulfur dyes is similar to the described above; the special principles involved have been presented under the headings following Indirect Dyes.

APPARATUS

Wooden tubs have been used for acid baths, but acid-resistant alloys such as Monel and Allegheny metal are finding wide usage, because of the ease with which traces of the dye can be removed when changing to another color. For neutral and alkaline baths, iron, steel and stainless steel are in common use. The dyeing may be done on skeins, or on the finished piece of material; in the latter case a device known as the jigger is used, shown in Figure 173a.

Thread, wound loosely on a spool having a perforated winding surface, is dyed by pumping the dye solution through the windings from the center

of the spool, and recirculating it until the bath is exhausted. This is known as the Franklin Process.

DESIGN FORMATION

Patterns in color may be produced on the piece goods by printing on copper rolls, using one of the three principles stated below.

1. In direct printing, the thickened dye solution is applied directly to the desired spot on the white piece goods; the remainder of the surface remains as before. For instance, a polka-dot design may be printed in blue from a copper roll having circular depressions filled with the dye solution. The blue dot on the white ground is formed directly. So that the color does not run at the edge of the dot, the solution is thickened by means of gelatin, starch, or other material.

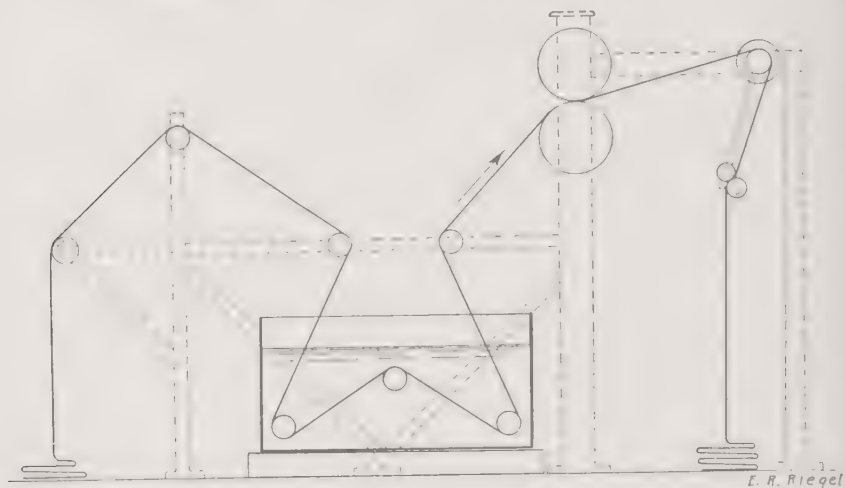


FIGURE 173a.—The jig.

Example on cotton: A basic dye mixed with tannin, acetic acid, and a thickener, is printed on directly; then the piece goods is steamed by passing it stretched over steam-heated hollow steel cylinders, washed, and dried.

2. In reserve printing, certain uncolored substances are printed onto the cloth at the spots which should remain white. The whole is then dyed. In the dye bath these substances repel the dye.

3. In the discharge method, the cloth is first dyed all over, and then there is printed onto it a substance which can destroy the dye by oxidation or reduction, leaving the spots reached by it uncolored. After the printing the cloth is steamed, washed, and dried.

As discharge materials, stannous chloride, zinc dust and caustic soda, bisulfite, sodium hyposulfite ($\text{Na}_2\text{S}_2\text{O}_4$), and others may be used, thickened properly by an inert material so that the applied discharge material does not run. Basic dyes are discharged by applying a paste of glucose, caustic soda, and a thickener; during the steaming, the reduction takes place.

Design formation by any one of these three methods is applicable to all fibers, with suitable modifications.

In Method 1 a mordant dye may be applied as well as a direct dye. It follows: The dye and the mordant mixed cold do not react appreciably.

two mixed with a thickener are applied. In the subsequent steaming, dye and mordant react, and fasten the produced lake onto the fiber.

In general, the printing is done with copper rolls etched in the design. In the depressions, the printing paste is fed constantly from a tank, while the surface of the roll is wiped clean by means of a scraper. This is a form of intaglio printing. The printing may be very elaborate; as many as 15 rolls have been applied to the same piece of cotton or silk.

Wetting-out Agents. In order to dye evenly, it is essential that the solution should reach every spot of the fiber at the same time; this will be the case only when the fibers are wetted at the same instant. The addition of certain substances favors this wetting, with subsequent even dyeing, and these materials have assumed an important rôle. The most important wetting-out agents are: soap, sulfonated castor oil, already mentioned, sulfonated naphthols, sulfonated abietene, Gardinol, Wet-It, Novo Naccosol.

Resin-treated Fibers. With the advent of modern plastics and resins, considerable use has been made of these materials to improve the tensile strength, resilience, durability, luster and firmness of fabrics. Some waterproof and weatherproof fabrics are attained by the application of a resin. The resin may be formed on the fiber or it may be applied directly, or by means of a solvent.*

Production. In 1940 there were produced in the United States 9600 million square yards of cotton; wool, 465 million pounds. For comparison, viscous rayon produced amounted to 257.1 million pounds; rayon staple, 145.5 million pounds; other artificial silks 132.9 million pounds.

PATENTS

U. S. Patent 1,865,701, manufacture of dyed rayon thread by precipitating the cellulose filament from a viscose solution impregnated with dyestuff in a reduced temperature and oxidizing the dyestuff to fix the color; 1,876,560, process of dyeing viscose rayon using tri-azo dyes. (R₁. N : N . R₁. N : N . R₂. N : N . R₃); 2,023,387; 1,998,550; 1,992,160; 2,000,559, wetting agent.

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- "Resins and plastics for the modification of textile fabrics," D. H. Powers, *Eng. Chem.*, 32, 1543 (1940); and several other articles on new textile fibers, and finishes in the same issue, p. 1547-1573.

The intermediates are the link between the low-valued products of the distillation of coal tar and the valuable dyes. The manufacture of dye intermediates is the most brilliant success of synthetic organic chemistry.

Chapter 27

The Manufacture of Dye Intermediates*

The group of synthetic compounds called intermediates is the starting point for the manufacture of dyes; they form the raw materials for the dye industry; to put it still another way, the intermediates are the foundations of dye constructions. The name is certainly appropriate, for they are intermediate compounds between benzene,¹ naphthalene, and anthracene, on the one hand, and the brilliant and varied dyes, on the other.

That benzene, naphthalene, and anthracene are obtained by distilling coal tar,² the evil-smelling black liquid found in the hydraulic main of an incinerating gas plant, and similar plants, has been stated in Chapter 14; hence the intermediates, "coal-tar intermediates," and the dyes made from them, "coal-tar dyes," as is often done, is therefore quite correct. In themselves, benzene, naphthalene, and anthracene are of little value; but the introduction of SO_3H , NO_2 , NH_2 , OH , alkyl or other groups into the molecule, replacing a hydrogen atom, the body becomes important and valuable; it is then an intermediate. The number of known intermediates is enormous; the number of the possible ones, greater still.

The transformation of benzene, naphthalene, and anthracene into these substituted bodies is done by a variety of operations, the most important of which may be divided into the following classes:

Nitration, the substitution of one or more hydrogens by NO_2 .

Reduction, for instance, of NO_2 to NH_2 .

Sulfonation, the substitution of one or more hydrogens by the sulfonic group, SO_3H .

Halogenation, the substitution of one or more hydrogens by Cl , Br , or I .

Alkylation, the substitution of hydrogen by an alkyl group, such as methyl, CH_3 , or ethyl, C_2H_5 .

Alkaline fusion, the substitution of the sulfonic acid group, SO_3H , by the hydroxyl group, OH .

In the discussion of these operations it is important to distinguish between various isomers produced, that is, bodies alike in the groups they contain, but differing in the relative position of these groups, as for example two nitrotoluenes shown below under Nitration. Such a distinction seems a rather nice one, belonging to the scientific aspect of the subject, but it is in reality of the greatest practical importance, because the dyes made later on by means of the separated isomers will differ. To obtain pure colors, an intermediate free from its isomers must be used.

*In collaboration with Robert Kuoch, Ph.D. (Basel), Consulting Chemist for Dyes, of Buffalo, N. Y. Benzene is the same substance as benzol.

²The greater part of the benzene is obtained by "scrubbing" the gas from the distillation of coal, and recovering it from the oil by distillation.

It naturally follows that a firm producing impure intermediates, in the sense that a given body is still accompanied by its isomers, is bound to see its business dwindle.

It might be said further that two isomers often differ in a pronounced way in their properties, although the structural difference is very slight. For instance ortho-nitrotoluene is a liquid, but para-nitrotoluene is a solid. The difference in properties is indeed sometimes slight, but there is always some difference in at least one property.

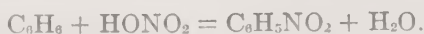
The compounds of carbon are exceedingly delicate; they react in many and always in several directions; for instance, while nitrating, some oxidation is almost unavoidable. This circumstance, added to the difficulty of isomer formation, renders the choice of processes and their supervision difficult that only men well-trained in scientific organic chemistry can carry out and supervise successfully. In no other branch of industrial chemistry do plant practice follow so closely the purely scientific treatment of the subject. Only the products of industrial importance and the well-established processes are considered in this chapter.

The apparatus is comparatively simple; wooden, cast-iron, and steel vessels are used. High temperatures are rare, which might be inferred from the fact that carbon compounds burn, and before burning are destroyed by charring; the temperature of melting ice is used almost as often as that of steam.

The system of notation in this chapter is the customary one: the symbol C_6H_6 means benzene, C_{10}H_8 means naphthalene, C_{10}H_8 . When a substituting group is written in place of a hydrogen atom is understood to have been removed to make room for the entering group.

NITRATION

Ordinarily, nitration is performed in the cold, in order to render less the oxidizing tendency of nitric acid. In many cases, the substance to be nitrated would be destroyed by nitric acid of full strength; to prevent this, it is diluted by means of concentrated sulfuric acid. This mixture is called "mixed acid,"³ and usually contains 25 to 30 per cent nitric acid, the rest is sulfuric acid with a small percentage of water. For example, the reaction for benzene is



Nitrobenzene, an oil, is formed, and water. The sulfuric acid does not enter into reaction, but serves as a diluent and an absorbent for the water formed during the reaction, thus maintaining the strength of the nitric acid.

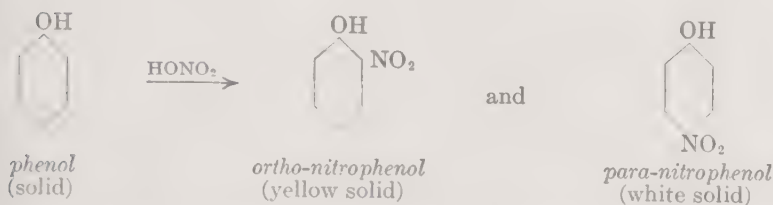
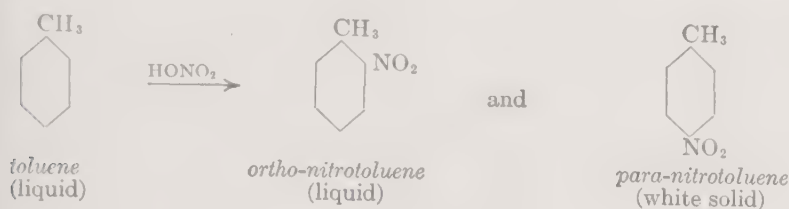
Not only are hydrocarbons such as benzene nitrated, but also, and frequently, substances in which there already are present other substituent groups. If the group NH_2 is present, it must be "protected" during nitration, even though the temperature is low, to prevent its oxidation and consequent loss. This "protecting" is done by acetylation, and the protecting group is removed after the nitration.

³ Chapter 2.

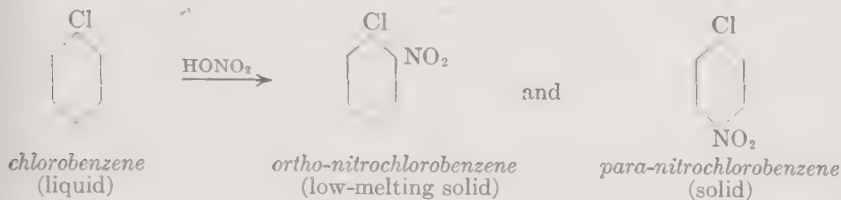
The groups already substituted in the molecule influence the position the entering group takes, according to the following rule, given in parts, with examples:

1. If any one of the groups CH_3 , CH_2Cl , Br , I , OH , NH_2 , and certain is present, the nitro group enters mainly in the ortho and para positions only in the para position.

Examples:



Ortho-nitrophenol and para-nitrophenol are isomers; they are separated by steam distillation, for the ortho body is volatile in the steam, while the para body is not, and therefore remains behind in the distilling vessel.



If there is present in the molecule any one of the following groups: COOH , CHO (the aldehyde group), or SO_3H , the nitro group enters only meta. Example:



When nitrating benzene to nitrobenzene, an excess of nitric acid must be avoided, otherwise dinitrobenzene is formed. The procedure is to run mixed acid into the benzene, not the converse; this is a general rule, if a single substituting group is desired. About 2500 pounds of benzene are nitrated in one batch, and the time is 3 to 4 hours. Heat is evolved during the reaction and is removed as fast as generated by means of cooling pipes.

laid in the benzene, or by means of cold water (or brine) circulated in the jacket surrounding the vessel; toward the end of the reaction, warm water is circulated in the jacket. (See Fig. 174.) Cast-iron is used, since nitric acid does not attack it. A stirrer is provided, for otherwise the benzene and the acid remain two separate layers. After the action is complete,

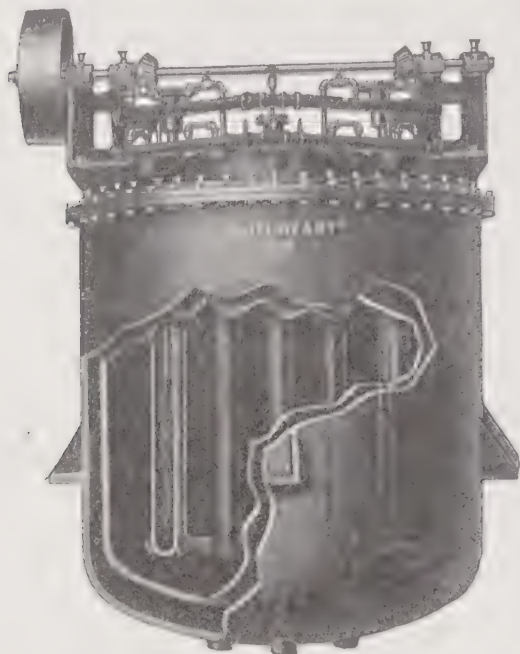
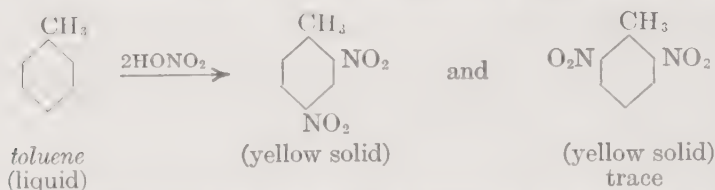


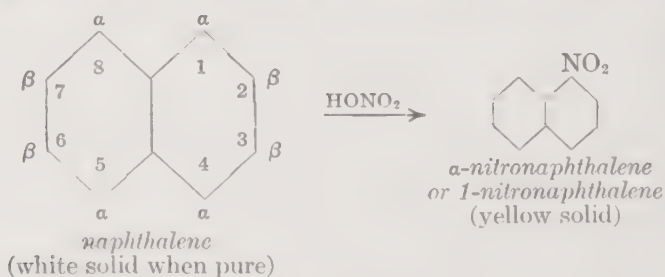
FIGURE 174.—Jacketed cast-iron nitration vessel, showing two impellers for agitation, and five cooling cells. (Courtesy of the Buffalo Foundry and Machine Co., Buffalo, N. Y.)

the nitrobenzene separates out as an oil over the acid, and is removed by decantation. It is agitated with water or dilute alkali to remove small amounts of acid, and may then be distilled if pure nitrobenzene is desired.

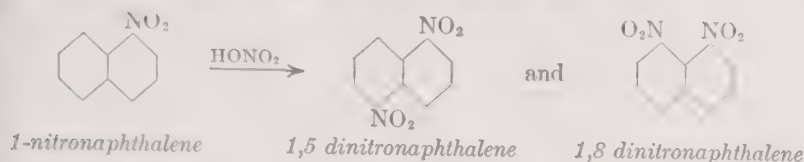
When nitrated with enough acid to form two nitro groups, toluene gives two different dinitrotoluenes; the temperature is kept at 35° C.:



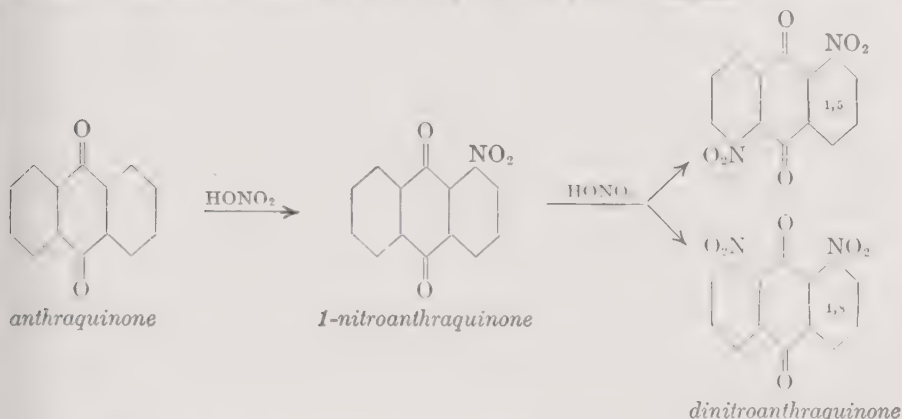
Naphthalene treated with the proper amount of mixed acid to form only one nitro group gives only α -nitro-, never β -nitronaphthalene:



Further nitration, the mono-nitro body gives 1,5 or 1,8 dinitronaphthalene; the temperature is 70° C.; all three bodies are solids.



Anthraquinone nitrated for one nitro group gives only α -nitroanthraquinone at 50° C.; a second group enters again α , producing the isomers 1,5 and 1,8 dinitroanthraquinone at 80° C.; all are yellow solids.

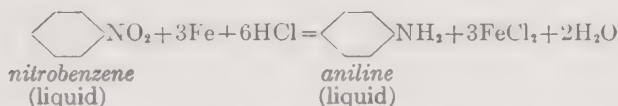


According to the amount of acid used, mono-, di-, or even trinitroanthraquinone compounds may be formed.

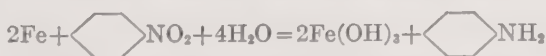
These nitrations are performed in cast-iron or steel vessels with steel agitators; a liquid requires no pre-treatment; a solid is dissolved in concentrated sulfuric acid, and this solution then treated with the mixed acid.

REDUCTION

Among reductions, that of the nitro group, NO_2 , to the amino group, NH_2 , is a frequent and important one; several reducing agents may be used: a. Iron turnings or powder and hydrochloric acid are generally used; b. frequently tin or zinc with hydrochloric acid. The theoretical reaction is



In practice, one-fortieth of the amount of acid required by this reaction is sufficient, because the ferrous chloride formed catalyzes the reaction:



When nitrobenzene is placed in the reducer, a vertical cylindrical vessel provided with cover, steam jacket and a stirrer; the iron turnings⁴ or powder

⁴ Cast-iron turnings, crushed in a hammer mill to pass through a 10-mesh screen, are to be preferred.

and the hydrochloric acid are added gradually, in small portions. A reaction, but not violent, is maintained by means of steam circulated in jacket, or blown into the charge directly. A condenser returns to jacket, or blown into the charge directly. A condenser returns to reducer any vapors which pass out. After the nitrobenzene is completely changed to aniline, a strong current of live steam is sent into the charge, a mixture of steam and aniline vapors passes out to the condenser and collected in storage tanks. The bulk of the aniline separates as a

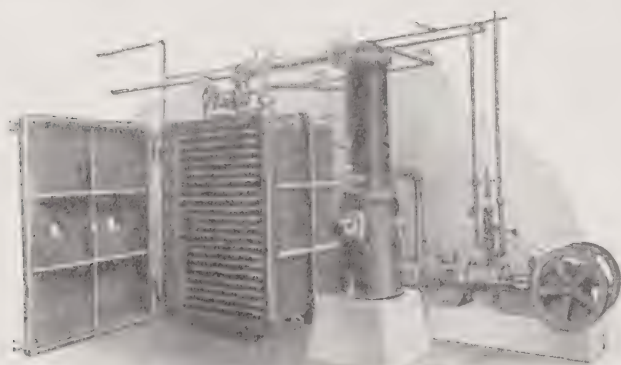


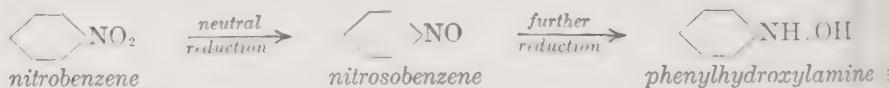
FIGURE 175.—A vacuum shell drier, with condenser and vacuum pump. The shell is hollow and receives steam. Such driers are used for intermediates and dyes (Bufflovak.) (Courtesy of the Buffalo Foundry & Machine Co., Buffalo, N. Y.)

layer and is drawn off; the water over it still contains aniline, which may be recovered by distilling this "aniline water" again, or by extracting it with nitrobenzene. The iron hydroxide sludge is washed out of the reducer through a side outlet by flushing. A reducer 6 feet in diameter and 10 feet high takes a charge of 5000 pounds of nitrobenzene in one batch. It requires about 10 hours for the reduction. The aniline may be redistilled when it is water white. There are many modifications of this method of reduction. The condenser consists of iron pipes laid in cold water.

Aniline is made from chlorobenzene, by treating the latter with ammonia in the presence of cuprous salts as catalysts. It is a continuous process with ammonium chloride as a rather annoying by-product.⁵

Aniline hydrochloride is a widely used white solid, and is made by treating aniline with hydrochloric acid.

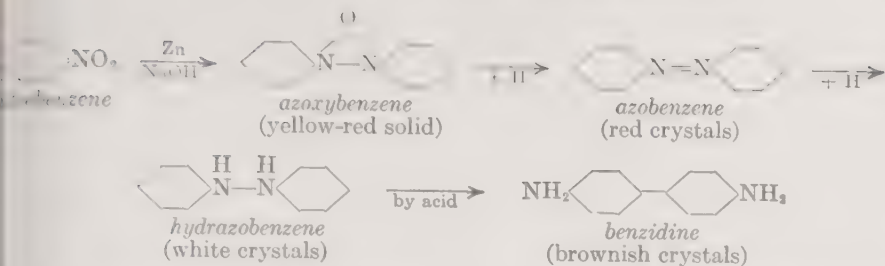
The reduction of nitrobenzene may be performed in acid, neutral, or alkaline solution and the products are in each case different. In acid solution, aniline is produced, as described above. In neutral solution, by means of zinc and ammonium chloride, phenylhydroxylamine results:



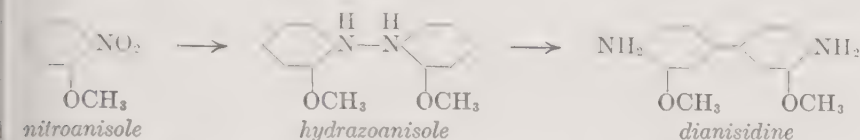
If the reaction is allowed to go too long, the phenylhydroxylamine is further reduced to aniline.

In alkaline solution azobenzene is formed, itself the starting point for benzidine:

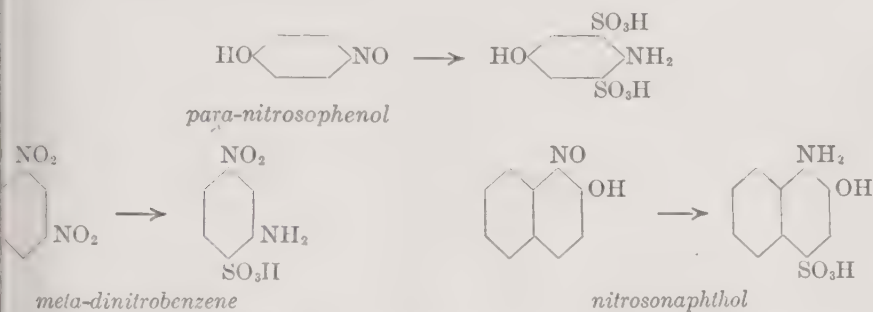
⁵ U. S. Patents 1,726,170-3; reissue 17,280.



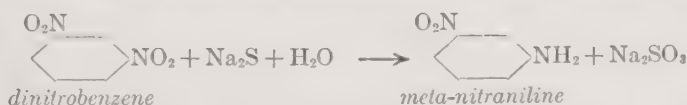
Alkaline reductions are performed, for instance, by means of zinc dust caustic in water, or in hydrous alcohol; in addition to the example we, the following may be given:



Sulfur dioxide as such, or its salt, sodium bisulfite, may be used for reducing, for instance, quinone to hydroquinone. When nitro or nitroso compounds are treated, the reduction is frequently accompanied by simultaneous introduction of the sulfonic group.



7. Sodium sulfide (Na_2S) is extremely valuable for reductions, as is also disulfide, prepared by dissolving sulfur in a solution of sodium sulfide. "partial reduction," that is, for the reduction of only one nitro group in a compound which has two, for instance, dinitrobenzene, sodium sulfide is usually chosen. The sodium sulfide is dissolved in alcohol and placed in



beam-jacketed reducer; the dinitrobenzene is added either solid, or also dissolved in alcohol. The mixture is maintained at boiling temperature for hours; then the alcohol is distilled off, condensed and collected in a similar reducer and is ready for the next batch; the loss of alcohol is slight. There remains in the first reducer the meta-nitraniline mixed with the organic salt; the mass is agitated with water which dissolves the salt. The

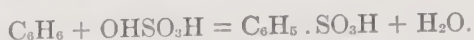
suspension is pumped into a filter press where the meta-nitraniline obtained as a moist cake; it is dried on trays in a vacuum drier.

The isomer, para-nitraniline, is made by nitrating aniline after protecting the amino group by acetylation; in other words, by nitrating the white solid acetanilide⁶; the temperature is maintained between 6° and 8° C.

SULFONATION

Sulfonation is performed to render insoluble compounds soluble in water or alkalies; or it may be performed as the first step in the introduction of a hydroxyl group, which is completed by subsequent alkaline fusion.

By direct sulfonation is meant the treatment of the substance with fuming sulfuric acid; in the case of benzene, an oleum containing 8 per cent free SO_3 is added gradually, to offset the dilution caused by the water reaction:



The temperature is maintained at 30° C. until near the end, when it is raised to 50°; the vessel used is shown in Figure 176. After the action is over

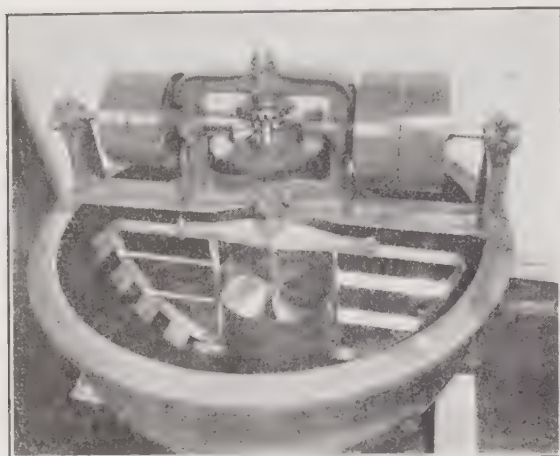
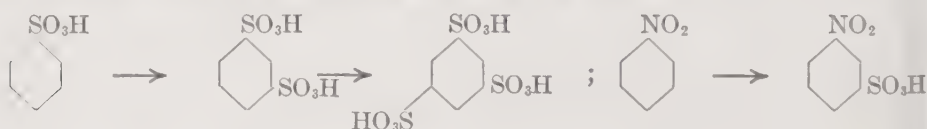


FIGURE 176.—A jacketed Doppelt sulfonator, with scraper and propeller. Positive scraping of surface cuts in half the time of cooling required when using propeller only. Scrapers on hollow shaft, low-speed; propeller on inner shaft, high speed. (Courtesy Sowers Manufacturing Co., Buffalo, N. Y.)

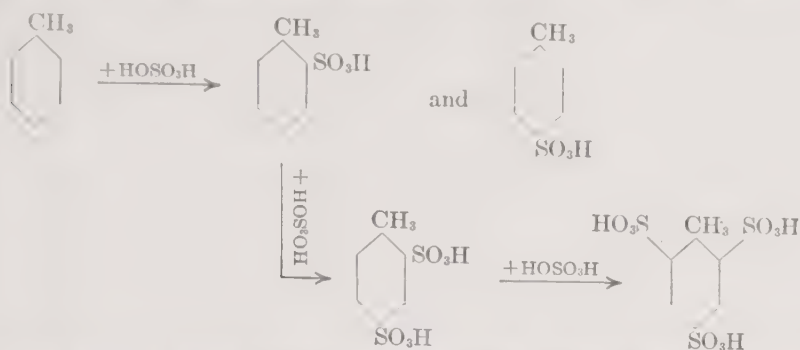
the charge is drowned in water, and the benzene sulfonic acid salted out; or, if the product is to serve for making phenol by alkaline fusion, lime is added; the free sulfuric acid is precipitated as sulfate which is removed by filtration. The liquor contains the calcium salt of the sulfonic acid; it is treated with soda ash, forming the sodium salt and precipitating calcium carbonate. After another filtration, the sodium salt in solution may be isolated by evaporation.

If there is present in the molecule one of the three groups, NO_2 , COOH , or SO_3H , the entering sulfonic group will take the meta position, in accordance with the rule for orientation given under nitration:

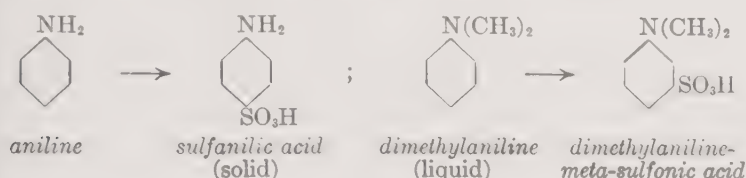


⁶ Another method is given under Halogenation.

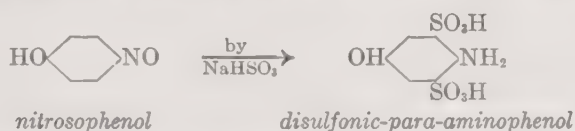
If the methyl group is present the result is different, but still in agreement with the rule; ortho and para derivatives are formed:



In sulfonating aniline, only para-sulfonic benzene, called sulfanilic acid, is formed; no protecting of the amino group is necessary; but if the aniline group is methylized, the sulfonic group enters meta:

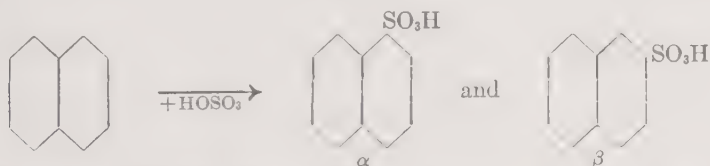


Indirect sulfonation may be done in various ways; for instance, bodies with the quinonoid structure may be sulfonated by NaHSO_3 , with simultaneous reduction of any nitroso or nitro group present to the amino group. Nitrosophenol is made by adding acid to sodium nitrite and phenol dissolved in caustic soda.



Reducing the same para-nitrosophenol with sodium sulfide (Na_2S), para-aminophenol is produced.

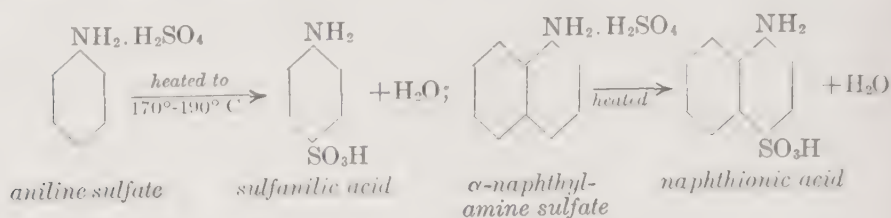
Direct sulfonation of naphthalene gives a mixture of α and β derivatives, varying the temperature; one or the other may be made to predominate; thus at 100°C . there are formed 95 per cent α and 5 per cent β ; while at 0°C . 18 per cent α and 82 per cent β are formed.



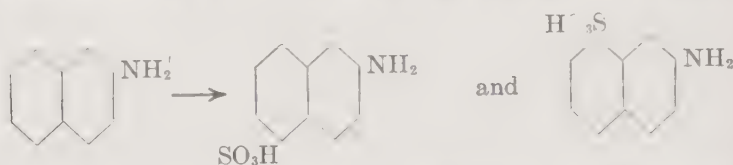
Naphthalene is melted and the acid run into it, to avoid the formation of disulfonic derivatives; the amount of acid is the calculated amount for one group. The water formed during the reaction retards but does not pre-

vent it; a definite amount of oleum (8 per cent SO_3) is added toward end in order to hasten it.

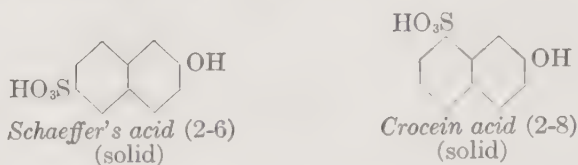
Sulfanilic acid and naphthionic acid are often prepared in an indirect way, namely, by forming the corresponding sulfate salt and heating the latter in thin layers, when an intermolecular change takes place and a sulfonic group enters the nucleus, in both cases in the para position; this is the "baking process."



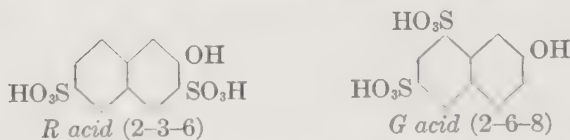
On direct sulfonation α -naphthyl amine gives mainly naphthionic acid; β -naphthyl amine forms a mixture of 2-5 and 2-8 sulfonic acids:



Sulfonation of β -naphthol yields two isomeric monosulfonic acids:



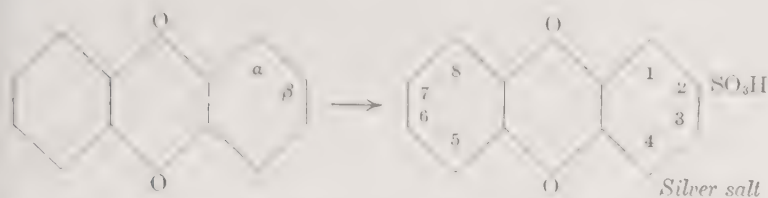
By further sulfonation two isomeric disulfonic acids form:



These two differ in that a diazo body couples with them at different rates; with the R acid, rapidly; with the G acid, slowly.⁷ Schaeffer's acid and Crocein acid show the same difference.

Anthraquinone, a yellow solid, is sulfonated by suspending it in oil containing 45 per cent free SO_3 (very strong oleum), and heating to 150°C . for one hour; the resulting melt is run into water and neutralized with caustic soda while hot. On cooling, the sodium salt of the β -sulfanthraquinone separates as a salt resembling metallic silver. For this reason it is called silver salt, important chiefly in the manufacture of alizarine.

⁷ R acid gives redder dyes, G acid dyes more on the yellow, hence the designations, from the German "rot" and "gelb."



On further sulfonation, a mixture of the 2,6- and 2,7-disulfonic anthraquinones is formed.

If the sulfonation is performed in the presence of mercurous sulfate, different products are obtained: a single sulfonic group enters at α or 1; two groups enter to form the 1,5- and 1,8-disulfonic anthraquinones.

HALOGENATION

Of the three halogens, chlorine is the most widely used, because of its comparative cheapness. As a rule, chlorinations are performed by dried chlorine gas, that is, by direct chlorination, with or without a catalyzing agent.

Chlorobenzene is made by passing a stream of dried chlorine into benzene in the presence of 1 per cent ferrous chloride; some paradichlorobenzene is formed at the same time:

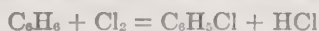


When passed into boiling toluene contained in a stoneware or enameled vessel, the chlorine enters the methyl group, producing a mixture of mono-, di- and trichlorotoluene, all liquids; dichlorotoluene treated with water in presence of calcium carbonate gives benzaldehyde; trichlorotoluene under the same treatment gives benzoic acid.



In this chlorination an iron vessel cannot be used, for the iron would cause evolution of the chlorine to enter the nucleus.

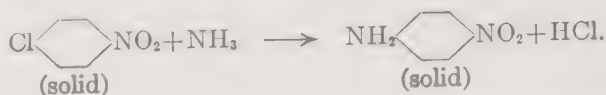
The hydrogen chloride formed in the chlorination might cause side reactions; in order to prevent this, in many reaction mixtures calcium carbonate is suspended. The calcium chloride which forms does not interfere.



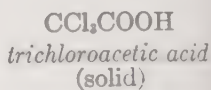
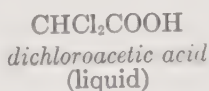
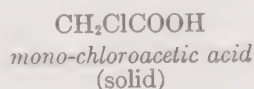
There are many catalytic agents in use such as SO_2Cl_2 (sulfuryl chloride), P_2Cl_5 (phosphorus pentachloride), SbCl_5 (antimony pentachloride), I_2 (io-

dine), Fe (iron); furthermore sunlight, ultraviolet rays, and temperature have an influence on the course of the reaction.

By means of the halogen, the reactivity of the compound is increased. The chlorine is more or less readily replaced by other groups. In the benzene or naphthalene nucleus, the chlorine is the more easily replaced. The greater the number of negative groups, such as nitro groups, present. Thus with ammonia, chlorobenzene does not react, but paranitrochlorobenzene does, forming para-nitraniline.



In acetic acid, one, two, or three of the hydrogen atoms in the methyl group may be replaced by direct chlorination of the warm liquid in the presence of sulfur:

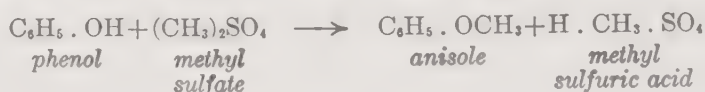


ALKYLATION

The alkyl groups, such as the methyl group, may be introduced into the amino group of an aromatic amine by heating it under pressure with methyl alcohol, in the presence of mineral acids.



Another method used at present is the treatment with methyl sulfate or ethyl sulfate in the cold, in presence of caustic soda:



ALKALINE FUSION

By means of an alkaline fusion, a sulfonic group is replaced by a hydroxyl group; there are other methods of introducing the hydroxyl group, but this is the simplest. The sulfonic acid is dissolved in a concentrated solution of sodium hydroxide or caustic in a covered cast-iron pot provided with a scraping stirrer and heated externally by steam, oil bath, or an open fire. The water is evaporated, and on continued heating, the mass fuses. The temperature varies for the various reactions, but lies between 250° and 350° C.

Phenol is manufactured by fusing benzene sulfonic acid with caustic soda. This reaction as well as two others are discussed in Chapter 35.



The sodium phenolate formed is treated with acid to liberate the phenol. Resorcinol is made by alkaline fusion:

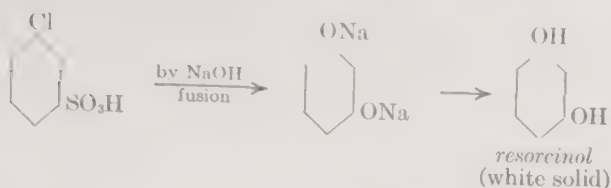
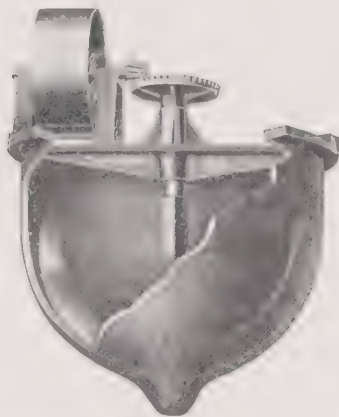


FIGURE 177.—Cast-iron fusion pot for alkaline fusions, with agitator.



β -naphthol is made by fusing the corresponding sulfonic naphthalene caustic; the naphtholate is treated with carbonic acid, and the prepared β -naphthol is purified by distillation in vacuum.

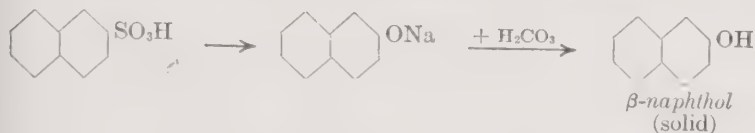
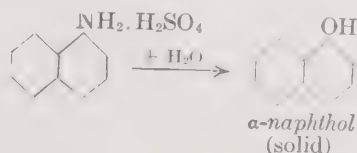


FIGURE 178.—A β -naphthol still.

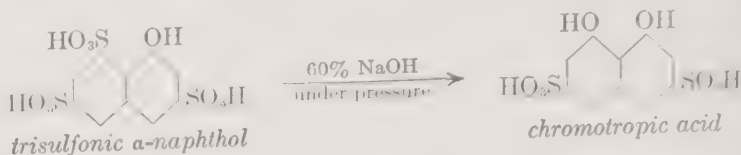
(Courtesy of Buffalo Foundry and Machine Company, Buffalo, N. Y.)



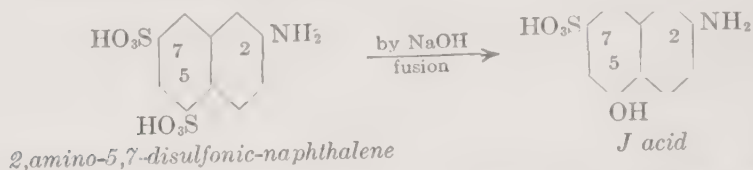
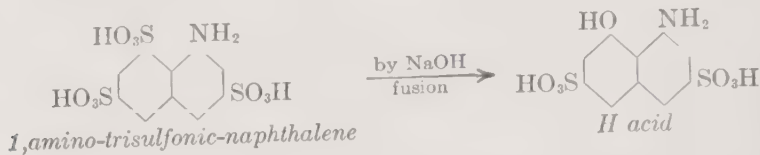
α -naphthol is not made from the sulfonic derivative, because some of the β -naphthol is always formed at the same time; instead, α -naphthyl amine is heated with excess water in closed lead-lined vessels to 200° C. for two hours. On cooling the α -naphthol crystallizes out.



Sometimes the action of the concentrated fused caustic is too great; in case a water solution is used and the reaction mix heated under pressure

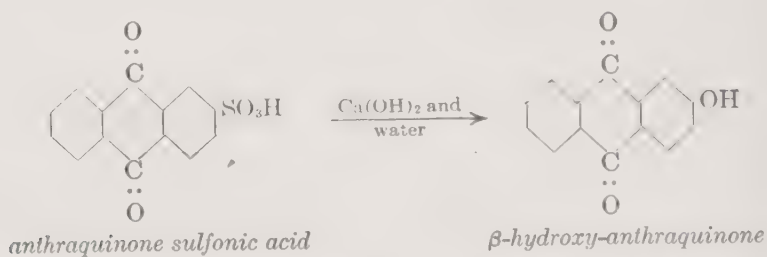


Sulfonated naphthyl amines may be fused with caustic to give aminonaphthols and aminonaphthol-sulfonic acids; the amino group is destroyed. Examples:

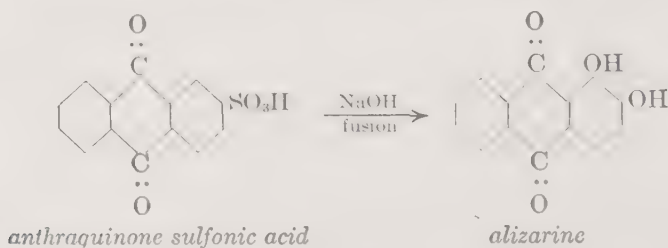


The aminonaphthol-sulfonic acids are almost indispensable for the manufacture of azo dyes; there is no azo dye of importance which does not contain at least one naphthalene derivative.

Antraquinone β -sulfonic acid may be changed to the hydroxyl compound by heating with milk of lime:

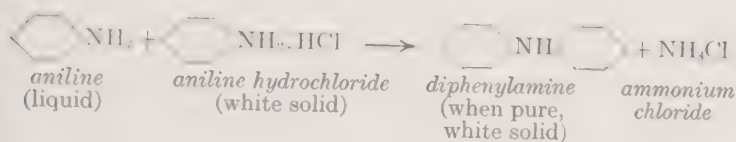


The same sulfonic acid fused with caustic gives the di-hydroxy derivative in addition to the mono-hydroxy compound. By adding an oxidizer as potassium nitrate or chlorate, a high yield of the dihydroxy anthraquinone forms; this is alizarine, which is discussed further in the chapter.

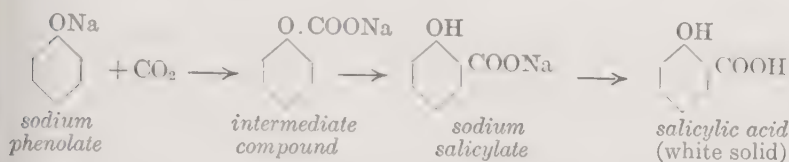


OTHER IMPORTANT INTERMEDIATES

Diphenyl aniline is made by heating aniline and aniline hydrochloride in a cast-iron vessel, an autoclave, for 32 hours at 200°C ; the melt is treated with weak hydrochloric acid, and distilled under reduced pressure. The body is important not only as an intermediate but also as a stabilizer for rayon-cotton.

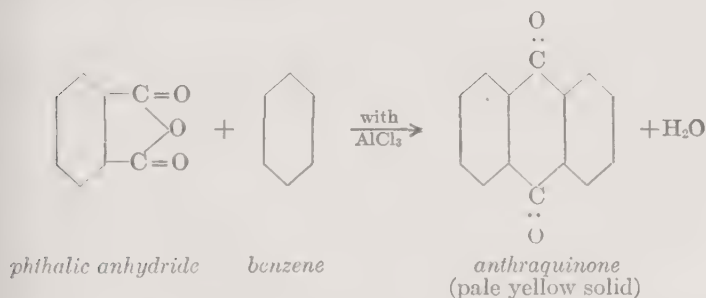


Salicylic acid is made by dissolving phenol in sodium hydroxide, evaporating to absolute dryness, passing in carbon dioxide under pressure, and maintaining the temperature near 150°C . in a cast-iron closed vessel. The mixture is dissolved in water, and acidified to precipitate the free acid, which is then purified by distilling at low pressure.



Anthraquinone is made by oxidizing anthracene with sodium dichromate and sulfuric acid. The crude anthracene, $\text{C}_{14}\text{H}_{10}$, is purified by pressing while warm; the press cake is atomized by steam, and the finely divided anthracene suspended in boiling water is treated with dichromate and sulfuric acid, added in portions. The mixture is run, while still hot, into water in order to dilute the acid; the anthraquinone is filtered and washed. Two methods for purification are given in Chapter 25.

By heating phthalic anhydride and benzene in the presence of aluminum chloride, anthraquinone is formed.



The intermediate compound containing the aluminum is first formed, and then, by removal of basic aluminum chloride, anthraquinone. Proportions for some typical intermediates are given in Table 69.

TABLE 69.—*United States production of a few dye intermediates and of raw materials for 1940.**

	Pounds	Price per pound
Nitrobenzene	69,105,449	
Naphthalene	58,249,891	6
Aniline oil	55,719,732	11
Dinitrochlorobenzene	9,753,665	
Dimethylaniline	7,049,741	
H acid	4,309,188	
Sulfanilic acid	1,941,126	
α -naphthol	0,558,859	
Total intermediates	805,806,899	15
	gallons	per gallon
Benzene (except motor benzene)...	36,555,643	12.9
Toluene	30,440,324	

* United States Tariff Commission, Report 148.

OTHER PATENTS

U. S. Patent 1,841,622, azo dye intermediates and the dyes therefrom; 1,834 production of dyestuff intermediates, di-anthraquinonyl derivatives containing chlorobromine and sulfonic acid groups in the 2-2 position; 2,029,315, trifluoromethyl-phenyl azo-diamino pyridines and process for making same.

PROBLEMS

1. 2500 pounds of benzene are nitrated in one batch, with a 90 per cent recovery to nitrobenzene which is then reduced to aniline by Fe and HCl. The aniline recovery based on the nitrobenzene is 88 per cent. How much aniline is obtained? How much Fe and HCl will be required?

2. Diphenyl amine is made by the process given in the text. In order to produce 1200 pounds every day, how much of the two raw materials will be needed? The recovery comes to 88 per cent. How much ammonium chloride will be left in the still?

From information obtained through the reading references, what size apparatus would you propose?

READING REFERENCES

"The manufacture of organic dyestuffs," André Wahl, translated from the French by F. W. Attack, London, G. Bell & Sons, Ltd., 1914.....

"Aniline and its derivatives," P. H. Groggins, New York, D. Van Nostrand Co., 1914.....

"Coal tar dyes and intermediates," E. D. B. Barnett in the series on Industrial Chemistry edited by Samuel Rideal, London, Baillière, Tindall & Co., 1914.....

"Equipment for nitration and sulfonation," R. Norris Shreve, *Ind. Eng. Chem.* 24, 1344 (1932).

"Intermediates for dyestuffs," A. Davidson, New York, D. Van Nostrand Co., 1914.....

"The synthetic dyestuffs and the intermediate products from which they are derived," J. C. Cain and J. F. Thorpe, London, Chas. Griffin and Co., 1933.

"Manufacture of dye intermediates," Arthur E. Pinkney, *Chem. Met. Eng.*, 45 (1938), describes quinizarine.

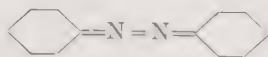
Natural dyes have been almost entirely displaced by synthetic organic dyes which supply every shade imaginable, and which have a brilliancy not approached by natural dyes. The intermediates discussed in the previous chapter form the components of the artificial or synthetic dyes; how these component parts are assembled will be described in this chapter.

Chapter 28

The Manufacture of Dyes*

An organic dye is a colored carbon compound which has the property of coloring permanently, with or without mordant, animal and vegetable fibers. Dyes are derivatives of carbon-containing radicals in which at least one ring structure, such as the benzene or naphthalene nucleus, is contained. Other chemical elements are present in the dye molecule, such as hydrogen, oxygen, nitrogen, and sulfur.

There are several classes of dyes, each of which contains one or more characteristic groups, a chromophore, such as $-N=N-$ for the azo class. An organic body containing the chromophore is a chromogen, such as benzene



introducing one or more of the following salt-forming groups (auxochromes), hydroxyl (OH), amino (NH_2), carboxyl ($COOH$), the chromogen becomes a dye.¹

The shades and nuances of the dyes depend, (a) on the nature and number of the chromophore and salt-forming groups, (b) on the relative disposition of these groups within the molecule. Generalizations are not easily made, but this much can be said for the azo dyes at least, that by increasing the number of chromophore and salt-forming groups, or by increasing the size of the molecule, the shade passes successfully from yellow to orange, red, violet, blue, green, and black.

Azo Dyes

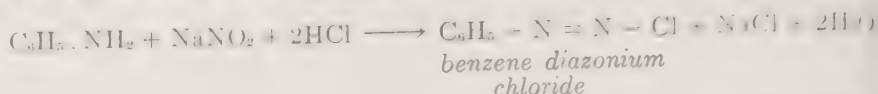
Azo dyes contain at least one diazo² group, the divalent chromophore $-N=N-$ combined with two aromatic radicals. The simplest chromogen in this class is azobenzene, which has weak coloring power; on introduction of salt-forming groups, the coloring power increases.

The main method³ of formation of diazo substances is by the "diazotization" of primary amines, followed by "coupling." Diazotization takes place when nitrous acid, HNO_2 , reacts on the primary amine group, NH_2 , attached to the benzene, naphthalene, or certain other nuclei, in the pres-

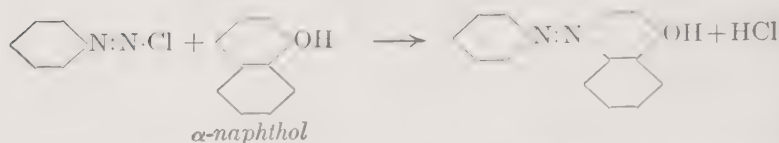
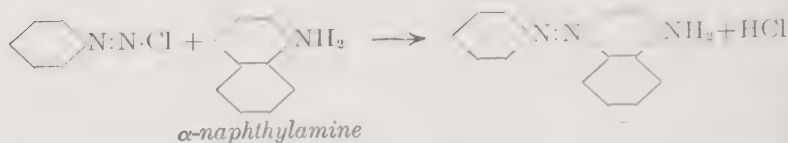
* In collaboration with Robert Kuech, Ph.D. (Basel), Consulting Chemist for Dyes, of Buffalo, N. Y. The hydroxyl and carboxyl form a sodium salt with caustic soda or soda ash, while the amino group forms a hydrochloride with hydrochloric acid.

¹ Diazo means two nitrogens, from azote, the French word for Nitrogen. Diazo is contracted to diazo, and that this latter expression also means two nitrogens in the form of $-N=N-$. Other methods are the reduction of nitro derivatives, and the action of a nitroso body on a primary amine.

ence of hydrochloric acid. Inasmuch as nitrous acid is unstable, its salt, NaNO_2 , is used, with an extra amount of hydrochloric acid.



Examples of coupling reactions with benzene diazonium chloride:



It will be noticed that the compounds with which the diazonium chloride reacts contain the salt-forming groups, OH or NH_2 . It is this property, possessed by the diazonium grouping, of combining with aromatic compounds containing one of these two salt-forming groups, which renders possible the formation of the numerous azo dyes. Certain general considerations may well precede the reactions for dye formation.

The diazo group does not enter at random, but in certain definite positions. The attack is generally in the nucleus, and one molecule of hydrogen chloride is eliminated. For the benzene derivatives, the attack is at the hydrogen para to the salt-forming group, or if that is occupied, at the ortho position; never in the meta position. Coupling in alkaline solution is rapid; in acid solution, slow. The alkaline solution must be used for phenols and substituted phenols, in order to form a solution; they are not soluble in water. The acid solution must be used for aniline and other amines, in order to bring them in solution. The alkaline solution removes the hydrogen chloride generated by the reaction as fast as it is formed; in the acid solution, such removal does not take place, unless sodium acetate is added, as is usually done; it is customary to hasten the reaction near the end by adding some soda ash.

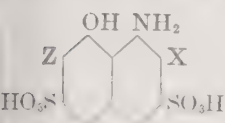
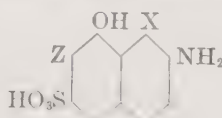
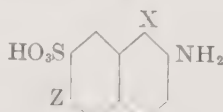
In the naphthalene derivatives, the orientation of the entering diazo group is somewhat different. In α -naphthol, the attack is at 4, or para; if that is occupied, the diazo group enters at 2, or ortho; as this is in agreement with the rule for benzene derivatives, it may be considered normal. In β -naphthol, the coupling takes place at 1; never at 3 and never at 4. The naphthols are coupled in alkaline solution.

*α-naphthol**β-naphthol*

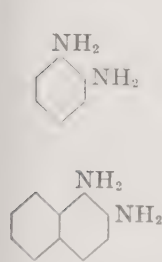
same position is taken by the diazo group when NH_2 replaces the hydroxyls; the substance is then a naphthyl amine, and the coupling is performed in acid solution.

The sulfonic group, SO_3H , is also a salt-forming group, but it does not have the power, when alone, to cause coupling. In the naphthalene derivative the presence of the sulfonic group in some cases influences the place of entry of the diazo group.

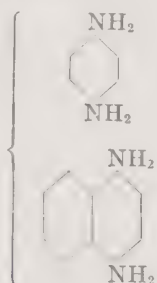
The carboxyl group, COOH , is also a salt-forming group; except in a few cases of no commercial importance, it does not cause coupling when alone. Certain aminonaphthol sulfonic acids couple twice, and in this case, the place of entry depends upon whether the coupling is performed in acid or alkaline solution. If in acid, the coupling is ortho to the amino group; if in alkaline solution, ortho to the hydroxyl. In the three samples following, the place of entry for acid coupling is marked X; for alkaline coupling, Z.

*H acid*⁴*Gamma acid**J acid*

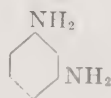
For these intermediates, too, alkaline coupling is rapid, acid coupling slow. *ortho*- and *para*-diamines in both the benzene and naphthalene series do not couple at all; only the *meta*-diamines do so.

*ortho-diamines*

do
not
couple

*para-diamines*

;

*meta-diamine*

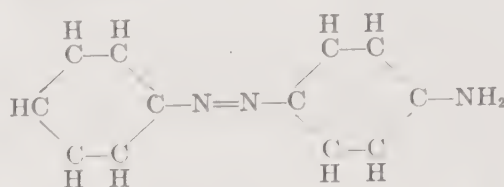
does
couple.

The procedure for diazotizing is to add at a slow rate a measured solution of sodium nitrite to the acid solution of the primary amine, in a wooden bucket provided with an agitator. By means of direct ice addition, the temperature is kept low, usually 0° to 5°C .; generally a solution results. The diazonium compound is not isolated, but the solution is run at once at a

It is recommended that the reader enter the formulas and names of the more important intermediates on a $5'' \times 8''$ card, and that he place this card next to the book while reading this chapter.

slow rate into the alkaline (or acid) solution of the intermediate with which the diazonium compound is to be coupled. After the addition of the diazonium compound, the batch is agitated for a period varying between 8 and 72 hours, until coupling is complete. The solution of the dye is warmed, solid salt (NaCl) is added and allowed to dissolve; on cooling, the dye separates out and is filtered in a plate-and-frame press. The apparatus is illustrated under Benzidine (p. 516).

Many of the compounds named in this chapter are described in the previous one and may be looked up there; the formulas of others are given in the proper place. It will be remembered that each corner of the benzene hexagon represents CH; where coupling has taken place, the hydrogen has been lost in the formation of hydrogen chloride, and its place taken by the diazo group. The full formula of the first azo dye, Butter Yellow, given in the next division, is therefore:



Mono-Azo Dyes. The mono-azo dyes contain the group $-\text{N}=\text{N}-$ once; the simplest example is aminoazobenzene, "butter yellow," soluble in oil and in butter; its use as a textile dye is unimportant. It is made by coupling diazonium chloride with aniline in acid solution⁵:



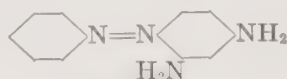
Butter Yellow

On sulfonating it with fuming sulfuric acid, Fast Yellow is formed, which is a mixture of the mono- and di-sulfonic derivatives:



Fast Yellow

Diazonium chloride coupled (acid) with meta-phenylene diamine gives Chrysoidine, which dyes a brown-yellow. The diazonium chloride, it will be remembered, is made by diazotizing aniline.



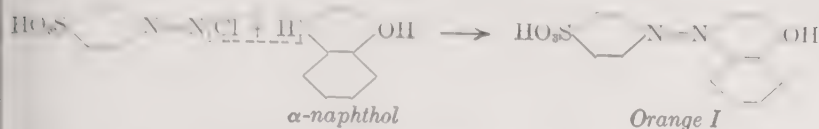
Chrysoidine

Sulfanilic acid



⁵ An intermediate step is omitted; there is first formed diazoaminobenzene $\text{C}_6\text{H}_5-\text{N}=\text{N}-\text{C}_6\text{H}_4\text{NH}_2$ and this rearranges itself under the influence of the acid into aminoazobenzene $\text{C}_6\text{H}_5-\text{N}=\text{N}-\text{C}_6\text{H}_5$. This intermediate compound is formed in every coupling reaction involving an

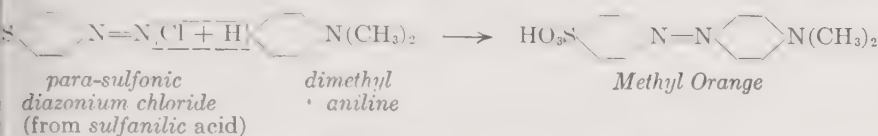
diazotized gives *p*-sulfonic diazonium chloride which may be coupled (line) with α -naphthol to form Orange I.



instead of α -naphthol, dihipenylamine is used, Orange IV results. Metanil Yellow is an isomer of Orange IV; it is made in the same way, that *m*-sulfonic aniline is the body which is diazotized.

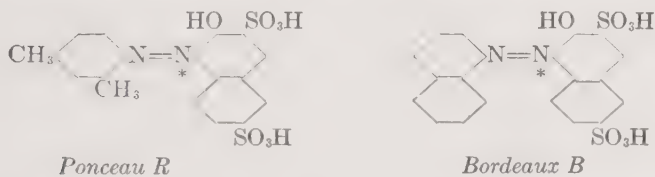


sulfanilic acid is diazotized and coupled with dimethyl aniline, Methyl Orange or Helianthine is obtained.



meta-xylylene, $\text{CH}_3-\text{C}_6\text{H}_3(\text{CH}_3)-\text{NH}_2$, diazotized gives the corresponding di-

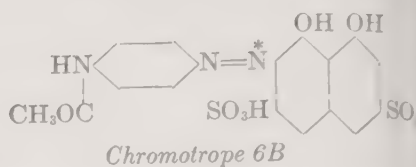
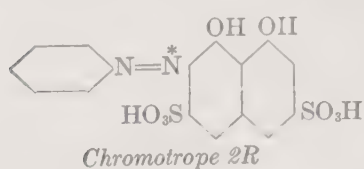
benzene-diazonium chloride; if the solution is run into an alkaline solution of R acid, Ponceau R, a wine-red dye, results. To avoid writing the formula twice, only the formula of the dye will be given, but the place of coupling will be marked by an asterisk; this will make it easy to recognize the component parts of the dye. It will be understood that a molecule of HCl is formed and removed at the place marked.* Bordeaux B, which dyes a deep red, consists of diazotized α -naphthylamine coupled (alkaline) with R acid.



Azo Rubine is made from diazotized naphthionic acid, coupled (alkaline) with Nevile and Winther's acid. Amaranth contains naphthionic acid again, this time coupled (alkaline) with R acid

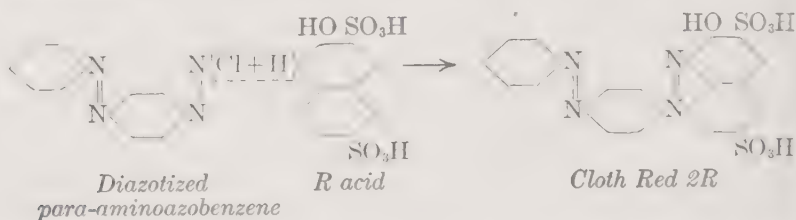


Chromotrope 2R consists of diazotized aniline coupled with chromotropic acid; Chromotrope 6B is *p*-aminoacetanilide coupled with the chromotropic acid.

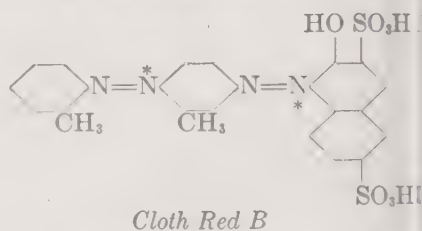
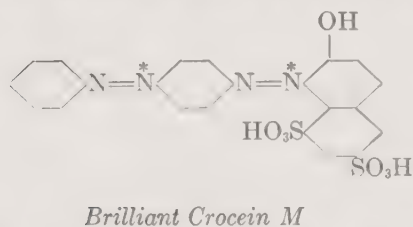


Secondary Dis-Azo Dyes. If an azo dye has been made with an intermediate which contains a free primary group, this group may be diazotized by treating the azo dye with sodium nitrite solution and hydrochloric acid; the resulting diazonium compound may then be coupled to a new intermediate, and a dye will result which contains two azo groups. Such a dye is a dis-azo dye, and, when prepared in this way, it is a secondary dis-azo dye. Primary dis-azo dyes are described later, under benzidine dyes. Some examples will be given.

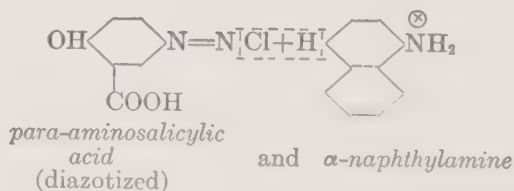
Para-aminoazobenzene or "butter yellow" is again the simplest case. It may be diazotized, and if then coupled with R acid, Cloth Red 2R is formed.



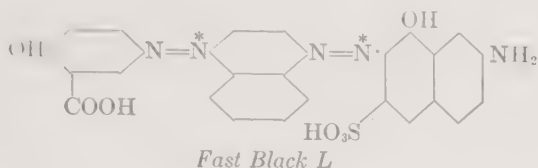
If the diazotized para-aminoazobenzene is coupled with G acid, Brilliant Crocein M results. Amino-azotoluene may be diazotized; and if then coupled (alkaline) with R acid, Cloth Red B is obtained.



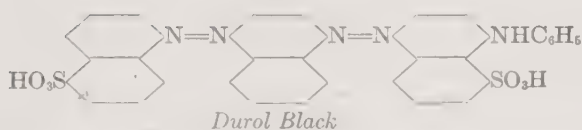
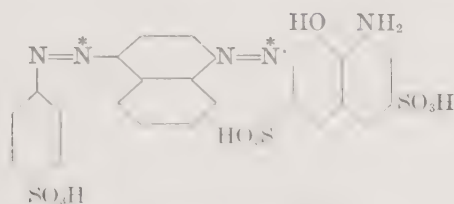
In the manufacture of Fast Black L, para-aminosalicylic acid is diazotized and coupled with α -naphthyl amine; the resulting compound, containing one azo ($-N=N-$) group, is diazotized again, and then coupled with Gamma acid.



ve a first dye. This first dye, treated with sodium nitrite and acid, the diazotized product (the new azo group forms at ²²) the solution of is poured into the alkaline solution of γ -acid.



aniline acid diazotized and coupled with α -naphthylamine gives a β -azo product which has a free amino group; this may be diazotized in turn and coupled with 1-amino-8-naphthol-3:6-disulfonic acid (II acid), black dye called Buffalo Black 10B results. Another black in this class is Durol Black.

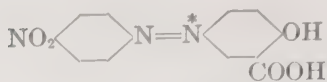


It will be observed that for these black dyes the molecule is large, and it contains in each case the grouping

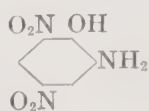
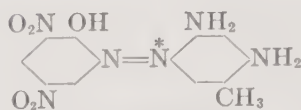


Mordant Azo Dyes. Certain azo dyes have the property of forming soluble "lakes" with metallic oxides; these lakes are fast to washing. The metallic oxides chiefly used are those of chromium and copper. The observation has been made that in order to form lakes, there must be present in the molecule a hydroxyl (OH) group with either a second hydroxyl, a carboxyl (COOH) or an azo ($-\text{N}=\text{N}-$) group in the ortho position to the hydroxyl; this observation is called a rule, and has already been given in a previous chapter. The following dyes are examples of such lake-forming dyes.

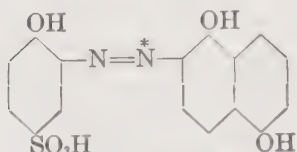
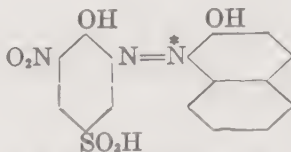
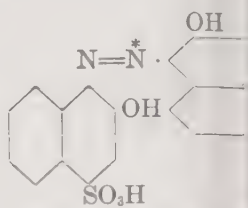
α -nitraniline diazotized and coupled (alkaline) with salicylic acid gives the so-called Alizarine Yellow, one of the simpler of the mordant dyes.

*Alizarine Yellow*

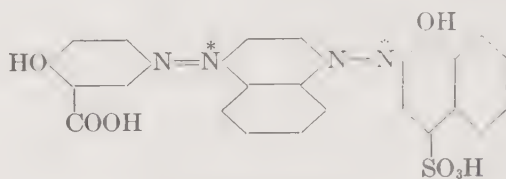
Another example is Chrome Brown, made by diazotizing picramine and coupling it (acid) with *m*-toluenediamine:

*picramine**Chrome Brown*

Still another example is Chrome Black PV, shown below; it is made by diazotizing ortho-aminophenol-para-sulfonic acid and coupling it (acid line) with 1,5-dioxynaphthalene. Two other important members of this group are Acid Alizarine Black and Palatine Chrome Black, whose constituent parts are sufficiently shown in the formulas:

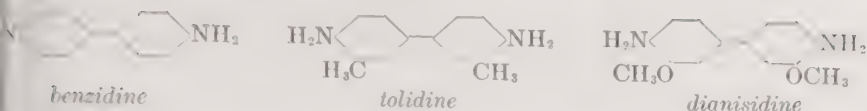
*Chrome Black PV**Acid Alizarine Black**Palatine Chrome Black*

Diamond Black F is a secondary dis-azo dye which is also a mordant dye; it contains salicylic acid, α -naphthylamine, and Neville and Nevill's acid.

*Diamond Black F*

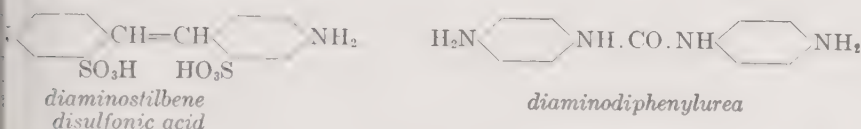
It will be noted that this dye has two lake-forming groupings.

Primary Dis-Azo Dyes. The azo dyes described in the previous divisions are mainly direct dyes for wool, or in the last division, mordant dyes for wool. Most of the primary dis-azo dyes in the present division are dyes for cotton, to which they are applied in the form of their sodium salts, which is also the form in which they are manufactured and shipped. These dyes are dis-azo, since they contain two azo groups; and they are primary, because the substance forming the starting point contains two primary amine (NH_2) groups; both may be diazotized, and both resulting diazonium groups may be coupled to some intermediate. Benzidine, a closely related substance is used for these dyes.



In addition to the primary dis-azo dyes there are tris-azo and tetra-azo dyes which are direct dyes for cotton.

The amino groups in benzidine may be diazotized simultaneously without being even partly destroyed by the nitrous acid, and without needing to be protected by acetylation. This property is shared by other substances, of which diaminostilbene-disulfonic acid and diaminodiphenylurea derivatives are of importance.⁶ The simultaneous diazotization of two amino groups is called tetrazotization, and the resulting product a tetrazo compound.⁷

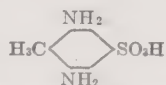


Benzidine in the free state is a brownish powder insoluble in water but soluble in dilute hydrochloric acid; both amino groups are diazotized simultaneously, and the resulting solution poured into the alkaline intermediate; the same intermediate is to be introduced at each azo group, two mols. of intermediate are used. The commercial procedure may be illustrated for Direct Blue 19, which is made by coupling benzidine with two molecules of H acid.



Benzidine is suspended in water in a wooden vat (Fig. 179); five mols.⁸ of hydrochloric acid are added, and the whole brought to a boil by passing steam. The required amount of acid is four mols, as indicated by the diazotizing reaction in the introduction to this chapter, two mols for each amino group; one mol is then the excess used. As soon as solution has taken place, ice is added, and a large part of the benzidine hydrochloride separates in a finely divided solid. Two mols of sodium nitrite, in solution in water, are run in gradually; for 184 pounds of benzidine (one mol) the addition of 138 pounds of nitrite (two mols) would require two hours. In the meantime 446 pounds (two mols) of H acid are dissolved in an excess of soda water (vat 3); to this, the contents of 2 are added, while stirring. When ice is added to keep the temperature at 5° C. The dye separates out in part; in order to separate it all, the contents of the vat are warmed.

4-Aminodiaminepara-sulfonic acid may be diazotized at both groups without protecting.



4-Aminodiphenylamine Nc1ccc(cc1)-c2ccc(N)cc2 cannot be diazotized at both groups without destruction. One mol is the number of grains or pounds numerically equal to the molecular weight.

by passing in steam through a movable pipe; solid salt is added and dissolved, and the contents are then cooled; all of the dye precipitates. The soda ash used with the H acid is sufficient to form the sodium salt of the

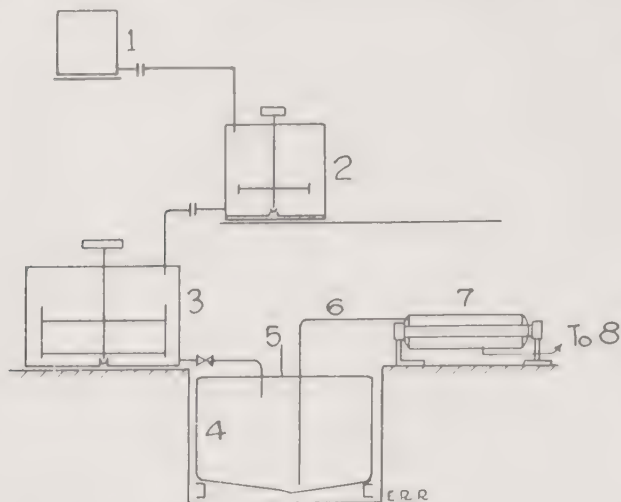
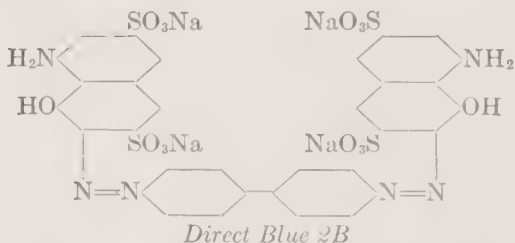


FIGURE 179.—Apparatus for manufacturing a benzidine dye; 1, sodium trite solution; 2, vat for tetrazotizing the benzidine hydrochloride; 3, vat for coupling; it contains the alkaline solution of H acid, to which the contents of 2 are added; 4, blow-case; 5, compressed air; 6, discharge line to press; 7, press; 8, vacuum drier.

The suspension is run into a wooden or an iron plate-and-frame press⁹; the filtrate is tested with more salt, and if exhausted, it is run to sewer. The cake is not washed, but merely freed from most of the adhering mother liquor by blowing with compressed air, while still in the press; the portion of the liquor retained must be removed by drying. The moisture is discharged onto shallow trays which are placed in a stationary vacuum drier wherein the moisture is removed at moderate temperature (70°C). The trays are placed each on a hollow steel shelf in which low-pressure steam or hot water is circulated. All dyes discussed in this chapter are solids, and are sold in the form of powders, or pastes.



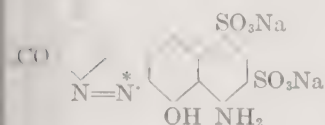
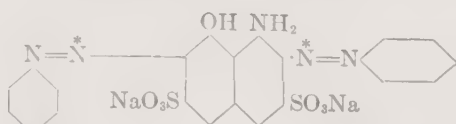
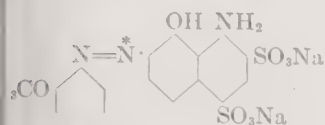
If it is desired to couple different intermediates at the two azo groups it is possible to do so because one group couples fast while the other couples slowly. By pouring one mol of the intermediate into the tetrazonium solution (the reverse of the usual order), one of the diazonium groups is coupled in each molecule; the second remains free,¹⁰ and may be coupled in a subsequent operation. In such a case one vat for each intermediate must be provided and must be placed at a higher level than the benzidine vat.

⁹ Chapter 42.

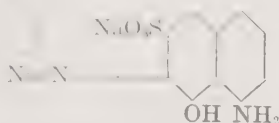
¹⁰ The end-point for the first group is found by touching drops of the solution on a filter wetted with an alkaline solution of R acid.

Direct Blue 3B is one shade bluer than the previous dye, and consists of the coupled twice (alkaline) with H acid.

Sky Blue FF is diamine tetrazotized and coupled twice (alkaline) with H acid.¹¹ Direct Blue NR contains tetrazotized benzidine coupled once (acid) with H acid, which has previously been coupled to diazotized phenol, and once with γ -acid (alkaline).

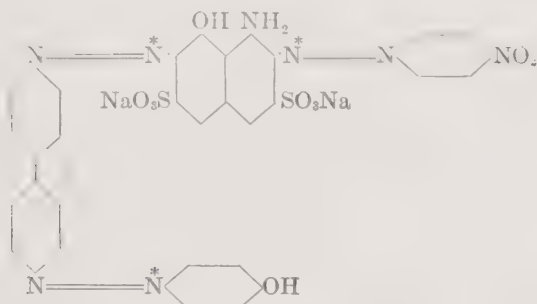


Sky Blue FF



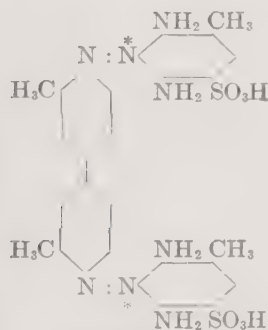
Direct Blue NR

A green dye is made by coupling tetrazotized benzidine with H acid (alkaline) which has previously been coupled (acid) with diazotized para-aniline, and at the second diazonium group with phenol.

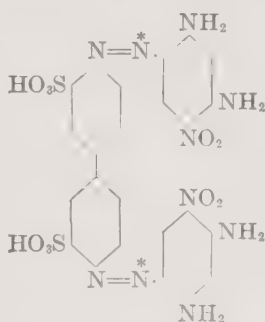


Direct Green

The composition of two orange dyes, two red dyes, a violet dye, and a blue dye (the last four on page 518) are exhibited by their formulas:

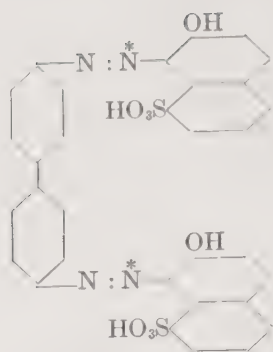
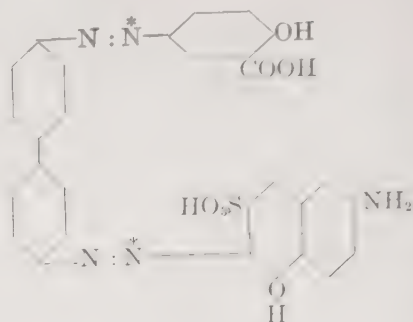


Toluylene Orange R



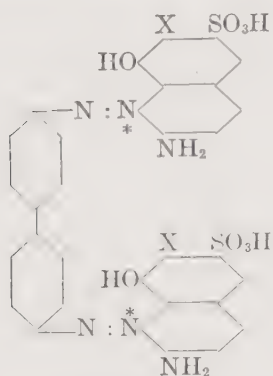
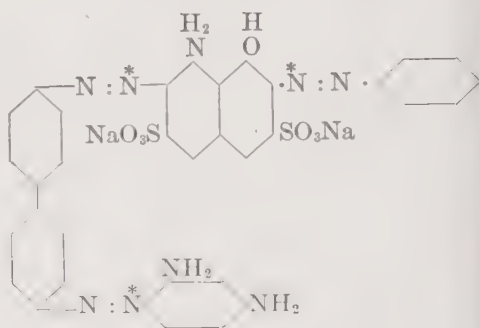
Pyramine Orange R

(-amino 2-, 4-disulfonic 8-hydroxynaphthalene.

*Bordeaux (red)**Direct Red J*

In Direct Violet, the γ -acid is coupled acid, as the place of entry of azo groups indicates; the coupling may be performed alkaline, where the place of entry will be adjacent to the hydroxyl group (at XX), and a slight difference in structure causes a blue dye to be produced, instead of a violet.

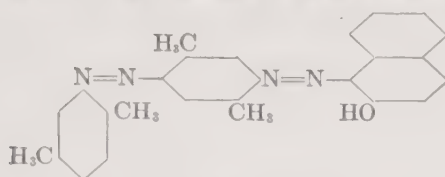
Stable Diazo Salts. A new development which is rapidly gaining is the manufacture of stable diazo salts, which consist of the uncoupled diazonium compounds in the form of its zinc, magnesium or tin salts. In forming the salt, the salted-out material is filtered and dried as there

*Direct Violet**Direct Black*

as possible on a suction nutsch. Next the cake is discharged and mixed with anhydrous potassium alum, or anhydrous magnesium sulfate, which takes up the remaining water in the form of water of crystallization. This is done because the diazo salt cannot be dried by heating, since it would be liable to explode. The dry diazo salt is shipped to the customer, who places it in a water solution, and passes cotton skeins or cloth through it. The dyes are wrung out, and sent through an alkaline naphthol (or other) bath, where that coupling takes place on the cloth. The result is a light-fast dye. It will be noted that the process resembles vat dyeing; it requires much less machinery, fewer chemicals, less skill, and less time.

The diazo compound is stable by virtue of the formation of its salt, hence the name.

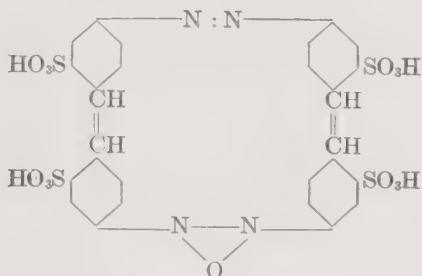
for Gasoline. In order to color gasoline red, a dye called Oil Red used, among others. Its formula will indicate that it is made by coupling aminoazoxylene, and coupling it with β -naphthol.



Oil Red EG

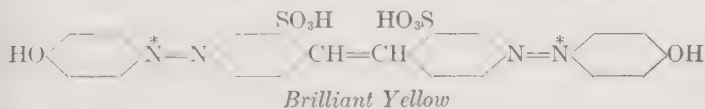
STILBENE DYES

stilbene dyes contain the chromophore $-N:N-$, not obtained how-
ever by diazotization of amines, but by the action of caustic soda on para-
toluene sulfonic acid. The colors formed by this reaction vary with
the amount of heating, temperature, and concentration of caustic, so that in
order to duplicate a color, the exact conditions must be observed. Little
known of the constitution of such dyes, and most of the brands on the
market consist of mixtures of products formed during the reaction.
The Mikado dyes belong to this group; Sun Yellow, shown below, is an
example:



Sun Yellow

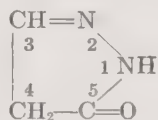
Another example of the stilbene dyes is Brilliant Yellow (used chiefly
for coloring paper); its formula is given below. Treated with ethyl chloride
($\text{C}_2\text{H}_5\text{Cl}$) under pressure, the two hydroxyls are changed to the ether
group (OH becomes OC_2H_5), and the more important Chrysophenine, a
yellow dye which is faster than Brilliant Yellow, is produced.



Brilliant Yellow

PYRAZOLONE DYES

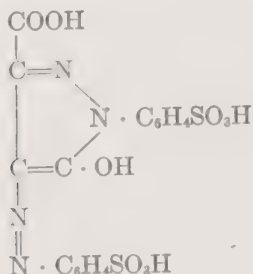
pyrazolone dyes contain the pyrazolone¹² nucleus



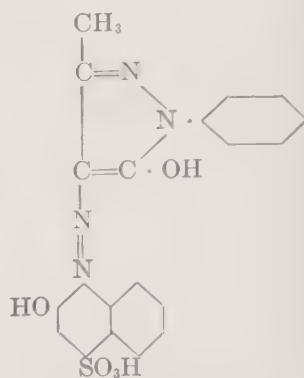
Acetyl-2,3 dimethylpyrazolone is antipyrine, a pharmaceutical.

Tartrazine, a favorite yellow dye, will be the example for this group, made by mixing a solution of 1 mol dioxy-tartaric acid¹³ and a solution of 2 mols phenylhydrazinesulfonic acid; on heating slowly, the dye forms.

Pyrazolone derivatives made from ethyl aceto-acetate condensed with phenyl hydrazine, para-sulfonic phenyl hydrazine, 3,6-dichlor-4-sulfonic phenyl hydrazine, and others, coupled with diazonium compounds of the benzene series, yield light-fast, clear yellows for wool. Coupled with a diazonium compound of the naphthalene series, a chrome red is formed; coupling takes place at 4.



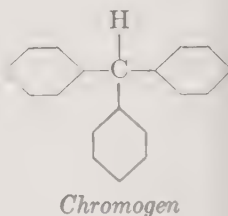
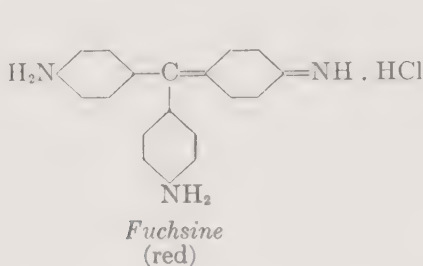
Tartrazine
(a yellow dye)



Eriochrome Red B

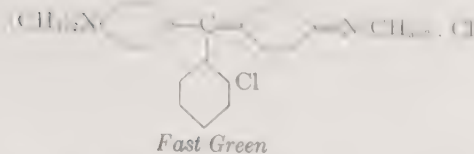
TRIPHENYLMETHANE DYES

Rosaniline, fuchsine, malachite green, and crystal violet are members of this class; its chromogen has three benzene nuclei attached to a central carbon, the so-called methane carbon, but one of the benzene structures has been altered to the quinone structure. The salt-forming groups are para to the methane carbon, and are usually the amino groups. Para-fuchsine is the simplest triphenylmethane dye; it is a hydrochloride. The chromogen is shown next to it.

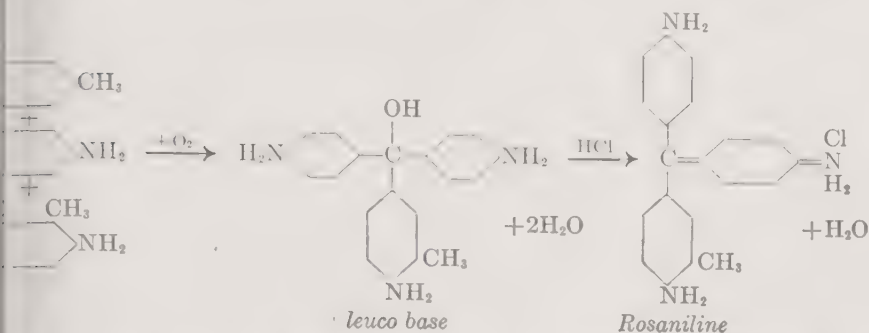


Fuchsine is the salt of a weak base; it is easily changed by alkali to a colorless carbinol. This property has greatly restricted its use; but fuchsine is present in the molecule, ortho to the methane carbon, the new dye is alkali-resisting. As example, Fast Green is given:

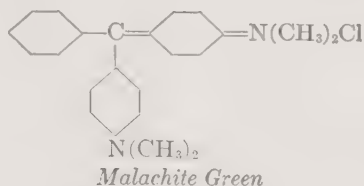
¹³ Made by oxidizing tartaric acid with nitric acid.



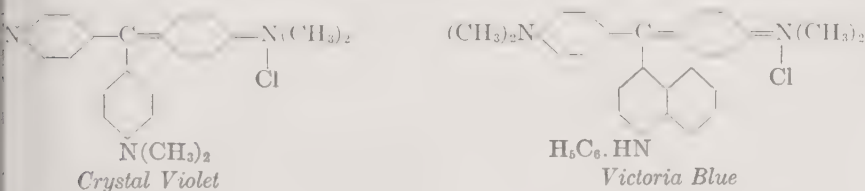
There are two methods of manufacture; one may be illustrated by rosaniline which is made by condensing 1 mol each of aniline, paratoluidine and toluidine in the presence of nitrobenzene as oxidizer. On neutralizing the resulting carbinol with hydrochloric acid, the dye forms.



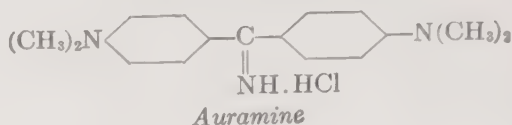
Another method involves the condensation of aromatic aldehydes, such as benzaldehyde, $\text{C}_6\text{H}_5 \cdot \text{CHO}$; monochlorobenzaldehyde, $\text{Cl} \cdot \text{C}_6\text{H}_4 \cdot \text{CHO}$; or ketones, such as Michler's ketone, $(\text{CH}_3)_2\text{N} \cdot \text{C}_6\text{H}_4 \cdot \text{CO} \cdot \text{C}_6\text{H}_4 \cdot \text{N}(\text{CH}_3)_2$, (made by passing phosgene, COCl_2 , into dimethylaniline, $\text{C}_6\text{H}_5 \cdot \text{N}(\text{CH}_3)_2$) with aromatic bases. Benzaldehyde (1 mol) condenses with dimethylaniline in the presence of zinc chloride to form a leuco base. On oxidation with lead peroxide and treatment with hydrochloric acid, it yields Malachite Green.



Condensation of ortho-chlorobenzaldehyde with dimethylaniline leads to Crystal Violet, with the formula as given above. Michler's ketone condenses in the presence of phosphorus pentachloride with dimethylaniline to a carbinol, which is changed by hydrochloric acid to Crystal Violet. The same carbinol condensed with a substituted α -naphthylamine gives Victoria Blue.

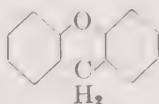


The diphenylmethane dyes are unimportant, except for Auramine low dye.

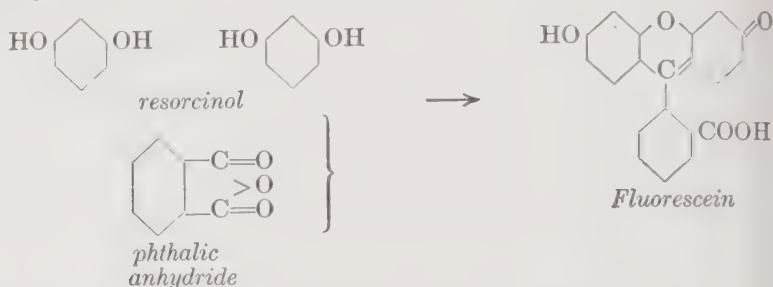


XANTHENE DYES

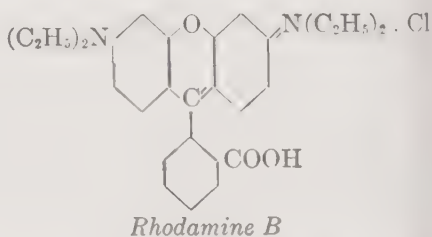
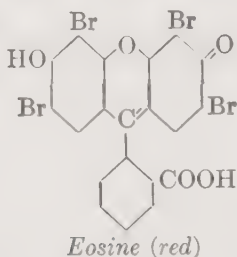
Fluorescein, eosine, and rhodamine represent each a series of dyes contain the same central structure, called xanthene, with the form



they are therefore classed together as xanthene dyes. Fluorescein is prepared by heating in an iron vessel phthalic anhydride (1 mol), resorcinol (2 mol) and zinc chloride; the temperature is regulated by means of an oil bath and kept at $220^{\circ}C$. for 7 hours. The melt is dissolved in caustic soda and the fluorescein precipitated by acidifying; it is a yellow-red dye. Its alkaline solution fluoresces green-yellow. Fluorescein itself is an important dye.



Dissolved in alcohol and treated with bromine while warm, four equivalents are absorbed to form tetrabromofluorescein or eosine.



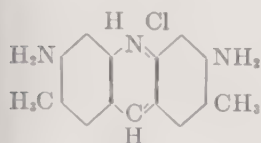
A number of other eosines are obtained by making dinitrodibromofluorescein and similar compounds, or their esters.

Erythrosine is a di- or tetraiodofluorescein; Phloxine the tetrachlorofluorescein.

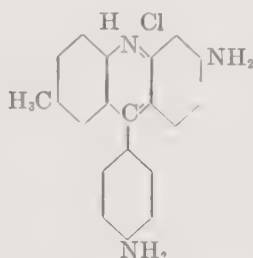
Rhodamines are made by condensing phthalic anhydride with substituted or ethylated meta-aminophenols in the presence of zinc chloride and treating with hydrochloric acid. Rhodamine B, a bluish-red dye, is the above.

me is a good mordant dye for cotton; it is made by condensing anhydride (1 mol) with pyrogallol, 1,2,3-trihydroxybenzene, (2

ted to the xanthene dyes are the acridines, azines, oxazines and s. Acridine Yellow results from the condensation of meta-tolulene- with formaldehyde, followed by oxidation and treatment with loric acid. Phosphine is a by-product of the manufacture of fuch- i is an acridine dye.

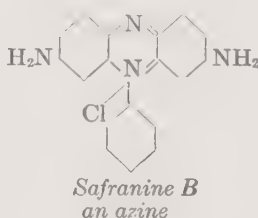
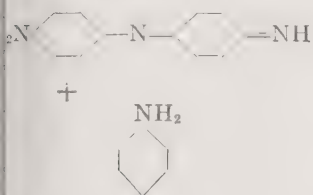
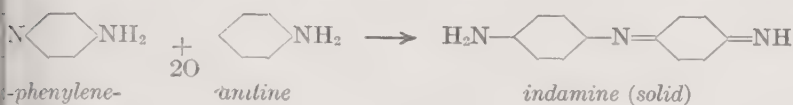


Acridine Yellow

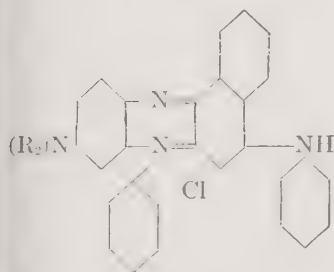


Phosphine

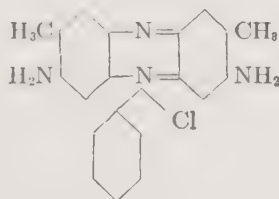
quinone-imide dyes, derivatives of indamine and indophenols, have listed separately because in themselves they are not important; require mention here because azine dyes are made from them. e is made from para-phenylenediamine and aniline; Safranin is an e. The azine nucleus has two nitrogen atoms in the central ring.



Safranin B
an azine

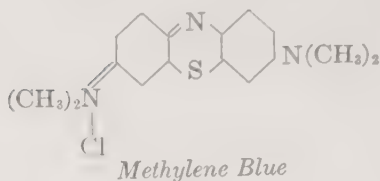


Wool Fast Blue GL and BL



Safranin

ylene Blue is a thiazine; its nucleus contains nitrogen and sulfur in al part:



On nitrating Methylene Blue, Methylene Green is formed. Methylene Green is an oxazine dye.

ALIZARINE DYES

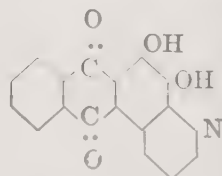
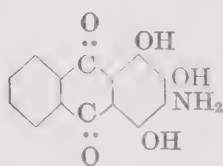
The alizarine dyes may be considered derivatives of anthraquinone, but some of them (for example Anthrarufin) are made by condensing benzene derivatives. Anthraquinone is the chromogen, which contains two chromophore groups, the two $>C=O$ groups; on introducing the salt-forming group, a dye results. With two hydroxyls at 1 and 2 (consult Chapter 27 for numbering), the dye is Alizarine proper, a mordant dye insoluble in water. If sulfonic groups are introduced besides, the dye becomes soluble, and is an acid dye. Alizarine is valuable as a dye in itself, but it is still so as the starting point of a large number of newer dyes of varied colors (Formulas in Chapter 27.) The sodium salt of β -sulfonic anthraquinone is called silver salt.

Alizarine is made by heating under pressure 100 parts of silver salt, so called because it looks like powdered silver, 250 to 300 parts caustic soda, 10 to 15 parts potassium chlorate, and some water, to $180^{\circ}C$. in a cast-iron or steel vessel provided with a slow-moving agitator. The reaction is an alkaline fusion, discussed in the previous chapter; but the hydroxyl groups introduced number one more than the sulfonic acid groups present. The resulting melt is dissolved in water, acidified, and the precipitated alizarine filtered and washed. It is sold in the form of a 20 per cent solution, it is used with mordants.

On sulfonating Alizarine, Alizarine Red is formed, a mixture of the mono- and disulfonic derivatives; this is now an acid dye.

Alizarine Orange is 3-nitro-alizarine; while Alizarine Brown is 1-nitro-alizarine, and when this nitro group is reduced, the dye formed is Alizarine Garnet (German Grenat).

Alizarine Blue is made from Alizarine Orange, β -amino anthraquinone, glycerin and sulfuric acid.¹⁴ Other alizarine dyes are Anthracene 1,2,3-trioxyanthraquinone, Purpurine 1,2,4-, Flavopurpurine 1,2,4-



¹⁴ The Skraup synthesis.

vanillic 1,2,5-trioxyanthraquinone. Alizarine Bordeaux is 1,2,5,8-anthraquinone. All these hydroxyl groups need not be introduced by fusion, for sulfonating with oleum of certain strength in the presence of boric acid or other substance, and subsequent water treatment, permits the introduction of the hydroxyl group and a control of its entry.

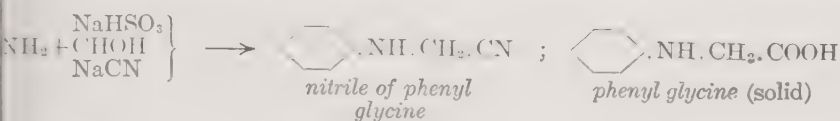
VAT DYES

A vat dye is insoluble in water, dilute acid or alkali; it must be reduced to a so-called leuco compound in order to be soluble, and it is only in this form that it has affinity for the fiber. The reduction was formerly done in the vat, hence the name, vat dyes. The reduction is performed with sodium hydrosulfite,¹⁵ a powerful reducer, or by zinc dust and sodium bisulfite; ferrous sulfide reduces only partly. After application to the fiber, the insoluble material reforms on exposure to the air by oxidation.

Vat dyes may be distinguished among the vat dyes: those which are (a) from Indigo itself, (b) from anthraquinone, and (c) other vat dyes which do not fit in a or b, such as Hydrone Blue.

The indigo group: Artificial indigo was synthesized originally from malic acid and chloroacetic acid, followed by several other operations; this procedure is now obsolete for indigo, but is still used for thio-indigo. A simpler procedure is simpler; aniline and chloroacetic give phenyl glycine, which condenses to indoxyl by fusion with alkali.

A really modern method is remarkably simple; it is a combination of the operations described in the patent literature. The first step is the preparation of phenyl glycine. In a water solution of sodium bisulfite, formaldehyde is placed; to this is added aniline oil, and then sodium cyanide. The reaction is formed in the cold, separated by filtration and washed free from the salt. The nitrile crystals are warmed in an alkaline slurry; ammonia is evolved, and a solution of the phenyl glycine salt is formed.¹⁶



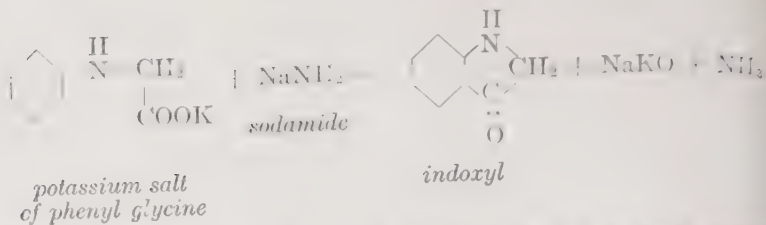
In the second step, the phenyl glycine salt is condensed by heating with a mixture of potassium and sodium hydroxide,¹⁷ in the presence of soda ash,¹⁸ which removes the water formed. The yield is excellent because the reaction temperature, 200° to 220° C., is much higher than in previous methods. The higher temperatures meant greater condensation of the indoxyl.

See 4.

German Patent 135,332, also 151,538.

German Patent 137,955.

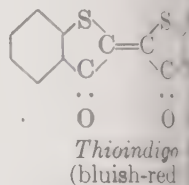
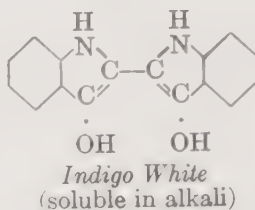
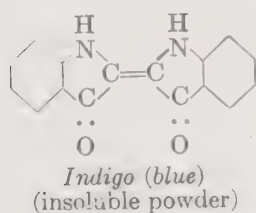
Soda ash is made by passing dry ammonia gas over melted sodium in a closed vessel, hydrogen gas being burned at a suitable outlet. $2\text{Na} + 2\text{NH}_3 = 2\text{NaNH}_2 + \text{H}_2$. Sodamide is a white solid at 120° C. German Patent 117,623. These four patents are reproduced in Friedlaender's (see reading references).



After the fusion, water is added, and in this alkaline solution blown; the indoxyl is oxidized to indigo, which precipitates and is off, washed, and dried. Two molecules of indoxyl form one of indigo the removal of 4 hydrogen atoms (as water).

Hydroxyethyl-aniline, formed when ethylene chlorhydrin is treated with aniline, is synthesized commercially to indigo with a molten mixture of potassium and sodium hydroxides containing ground calcium oxide; hydrogen is evolved. The thioindigos are made from phenyl thioglycine derivatives.

In order to apply indigo to fibers, it is reduced to indigo white, which is soluble in alkalis.



Of the halogen derivatives, known commercially as Brilliant Indigos, those containing bromine give increasing green shades, while the indigos lie between indigo and bromindigo in brilliancy.

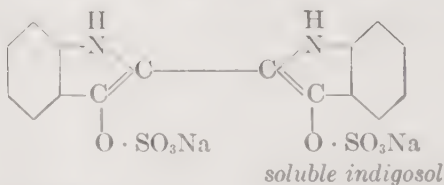
Bromindigos are prepared by the direct bromination of indigo with liquid bromine in a ball mill, or by refluxing in nitrobenzene.

The direct chlorination of indigo is performed in glacial acetic acid or nitrobenzene suspension, and is less simple.

Indigo is produced in the form of a 20 per cent paste, for domestic and export consumption. In 1930, 24,327,000 pounds of synthetic indigo were produced in the U. S.; in 1940, much less, 11,133,161 pounds.^{15a}

Indigosols (IG), Soledons (ICI). These are new developments in the Indigoid and Vat classes of dyestuff, and are popular because of their application compared to the usual vat dye methods. They are dissolved in water and are applied to the fiber. The fiber is then treated with an acid oxidizing liquor which develops the true vat dye in the fiber.

Indigo, for example, is applied in the form of soluble indigosols

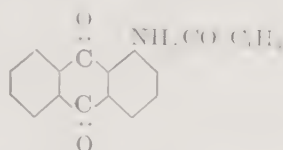


^{15a} U. S. Tariff Commission, reports on Dyes.

* Brit. Patents 186,057; 313,407; 503,699.

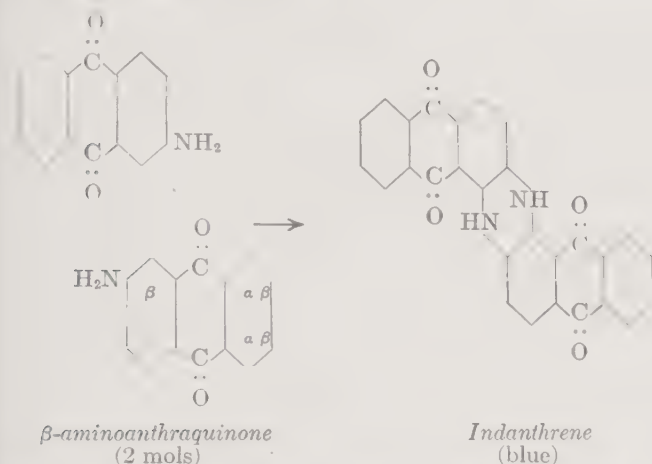
en is treated with a solution of sodium nitrite or sodium bichromate reverts to the insoluble form of indigo.

The anthraquinone vat dyes are made from α - or β -amino-anthraquinone. α -aminoanthraquinone may be made by direct nitration followed by reduction; β -aminoanthraquinone must be made by an indirect method; sulfonic anthraquinone is treated with ammonia under pressure. The most important of these dyes is Algol Yellow.

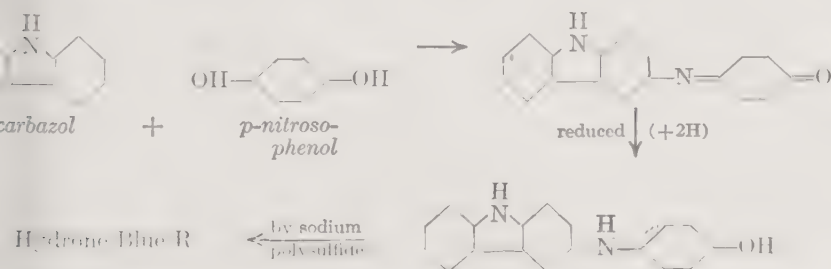


Algol Yellow

By heating β -aminoanthraquinone with caustic potash, Indanthrene is formed, a beautiful blue vat dye which is the fastest dye known at present. To this class belong also Flavanthrene (yellow), Indanthrene Gold Orange, and the important phenanthrones.



Hydrene Blue is a class of sulfur dye which may be reduced by hyposulfite $\text{Na}_2\text{S}_2\text{O}_4$ without destruction, unlike the typical sulfur dyes. In order to prepare Hydrene Blue R, para-nitrosophenol is condensed with carbazol in the presence of sulfuric acid at a definite temperature. The product is fused with alkali polysulfide. The formula of the dye is fully known.

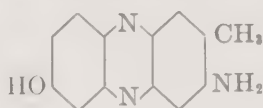


Hydronic Blue G is made from ethyl carbazol ($\text{—N—C}_2\text{H}_5$ instead of N—H) by condensing it with *p*-nitrosophenol; it gives a greener blue than Hydronic Blue R. Like the other vat dyes, Hydronic dyes must be reduced (sodium hyposulfite $\text{Na}_2\text{S}_2\text{O}_4$) in order to apply them to the fiber.

SULFUR DYES

The sulfur dyes are insoluble in water; they are reduced by sodium hydride and thereby become soluble, so that they can be applied to the fiber. They are reoxidized to the insoluble compound on exposure to the air. Their constitution is essentially unknown, but the proper raw materials and conditions for obtaining definite colors are fairly well settled.

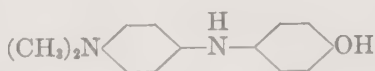
Meta-diamines, for instance meta-phenylenediamine, fused with sodium polysulfide, causes the evolution of hydrogen sulfide and a melt is obtained which yields brown and yellow dyes. Redder shades are obtained by using derivatives of azine; thus the methyl-aminooxyazine shown below,



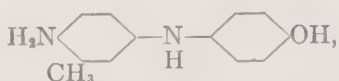
fused with polysulfide in presence of a copper salt, gives a Bordeaux blue.

Blue shades are obtained by treating diphenylamine derivatives in alcohol solution with sodium polysulfide, which will be only partly dissolved; a water solution may be used also.

From



there is obtained Immedial Sky Blue. By condensing nitrosophenol with ortho-toluidine in 80 per cent sulfuric acid there is formed the body



which treated with polysulfide in alcohol gives Thionone Blue. Similar to the condensation product of nitrosophenol and diphenylamine, with the following formula



yields Pyrogene Indigo.

On refluxing in water or by heating under pressure meta-dinitrophenol ($\text{HO—C}_6\text{H}_3(\text{NO}_2)_2$) with polysulfide, Sulfur Black is formed.

In order to isolate the dye, the procedure is to dissolve the melt in water and blow in air till all the dye has separated; it is filtered, washed, and dried in vacuum driers.

DYES FOR SYNTHETIC RESIN PRODUCTS

spirit-soluble dye is made by adding to a water solution of a dye an acid solution of diphenylguanidine.¹⁹ The dye treated may be directly soluble in water, or may require acidification for solution. The dyes which are suitable for this transformation must be found by trial; they belong to a number of classes. In order to bring about the reaction, the bath may have to be heated to boiling, or it may not require any heating. A precipitate is formed which is usually tarry. The clear liquid is decanted, and the tar removed preferably under reduced pressure. Extensive use is made of these soluble dyes for coloring synthetic molding resins, for which they are well adapted, as they dissolve readily in them.

It is not possible to tell which dyes will be suitable for the diphenylguanidine treatment can be told before a trial; the only general statement which can be made is that any dyestuff containing an acid group in its molecule, so that its sodium salt will be water-soluble, is worth a trial (acid colors, direct colors, chrome colors, and certain eosine dyes).

Other dyes suitable for use with synthetic resin products are found among the oil-soluble dyes, azo or anthraquinone dyes without the salt-forming and solubilizing groups SO_3H and COOH and others.

The bases for Celanese dyes can be used in cellulose acetate plastics, giving clear brilliant shades.

Permitted Coal-Tar Food Dyes. The "Food, Drug and Cosmetics dyes" are used for the artificial coloring of foodstuffs and beverages, provided they contain a minimum of 82 per cent of the pure coal-tar dye, and only a small amount of specified impurities and moisture make up the remaining 18 per cent. The tests which must be used to establish the presence, absence, or quantity of the impurities are those which are published in the official bulletin.²⁰ A selection of F. D. & C. items follows:

No. 1, or Ponceau 3R $\text{C}_{18}\text{H}_{13}\text{N}_2\text{S}_2\text{Na}_2$, a mono-azo dye, made by diazotizing 1-cumidine and coupling with R acid; a dark red powder, giving a cherry water solution.

No. 4, or Ponceau S X $\text{C}_{18}\text{H}_{11}\text{N}_2\text{O}_7\text{S}_2\text{Na}_2$, a mono-azo dye, formed by coupling diazotized 1-amino-2,4-di-methylbenzene-5-sulfonic acid with 1-naphthol-4-sulfonic acid; a red powder, which dissolved in water gives red.

No. 2, or Amaranth $\text{C}_{20}\text{H}_{11}\text{N}_2\text{O}_6\text{S}_2\text{Na}_2$, a mono-azo dye, made by diazotizing 1-naphthol-4-sulfonic acid and coupling with R acid; a reddish-brown powder, giving a magenta-water solution.

No. 3, or Erythrosine $\text{C}_{20}\text{H}_8\text{O}_6\text{I}_4\text{Na}_2$, the sodium salt of tetraiodofluorescein, a red powder, which in water gives a cherry-red solution without fluorescence.

No. 1, or Orange I $\text{C}_{18}\text{H}_{11}\text{N}_2\text{O}_3\text{S}_2\text{Na}_2$, a mono-azo dye, made by coupling diazotized sulfanilic acid with α -naphthol; a reddish-brown powder, dissolving in water gives an orange-red solution.

No. 6, or Sunset Yellow F C F $\text{C}_{18}\text{H}_{13}\text{N}_2\text{O}_7\text{S}_2\text{Na}_2$ is a mono-azo dye, formed by coupling diazotized sulfanilic acid with β -naphthol-6-monosulfonic acid; the powder is orange-red, and dissolves in water to give an orange-yellow color.

No. 1, or Naphthol yellow S $\text{C}_{19}\text{H}_7\text{N}_2\text{O}_5\text{S}_2\text{Na}_2$, a nitro dye, is the sodium salt of 2,4-dinitro- α -naphthol-7-sulfonic acid; a light yellow powder which in water gives a yellow solution, unaltered by either acid or alkali.

¹⁹ U. S. Patent 1,674,128.
²⁰ Bulletin 1396 and supplement No. 1, "Chemistry and analysis of the permitted coal-tar food dyes," by Joseph A. Ambler, W. F. Clarke, O. L. Evenson, and H. Wales, Color Laboratory, Bureau of Chemistry, U. S. Dept. Agriculture, 1927-1930. Since the passage of the Federal Food, Drug and Cosmetic Act, May 4, 1939, the dyes are designated by number, as shown; see Federal Register, vol. 4, p. 1922, Washington, May 9th, 1939.

Yellow No. 5, or Tartrazine³ $C_{16}H_8N_2O_5S_2Na_2$, a pyrazolone dye, is an orange powder, soluble in water.

Yellow No. 3, or Yellow A. B. $C_{16}H_{11}N_3$, an oil-soluble mono-azo dye, is a coupling diazotized aniline with β -naphthylamine; insoluble in water.

Yellow No. 4, or Yellow O B $C_{17}H_{15}N_3$, an oil-soluble mono-azo dye, is a coupling diazotized ortho-toluidine with β -naphthylamine; it is insoluble in water.

Green No. 1, or Guinea Green B $C_{27}H_{30}N_2O_6S_2Na_2$, a triphenylmethane dye, is formed by condensing benzyliethylaniline-sulfonic acid with benzaldehyde, oxidizing, and converting the resulting product to the mono-sodium salt. It is a dull dark-green powder, dissolving in water to give a green solution.

Green No. 2, or Light Green S F Yellowish $C_{27}H_{34}N_2O_6S_2Na_2$, a triphenylmethane dye, has the composition of Guinea Green B with an additional sulfonic acid; it is a reddish-brown powder which in water forms a green solution.

Green No. 3, or Fast Green F C F* $C_{27}H_{34}N_2O_6S_3Na_2$ is a triphenylmethane dye which is formed by condensing benzyliethylaniline-sulfonic acid with para-ortho-sulfobenzaldehyde and oxidizing the resulting product. It is a reddish or bluish-violet powder, which when dissolved in water gives a bluish-green solution.

Blue No. 1, or Brilliant Blue F C F $C_{27}H_{34}O_5S_2N_2Na_2$, the disodium salt of a triphenylmethane dye formed by condensing benzaldehyde-ortho-sulfonic acid with benzyliethylaniline-sulfonic acid; it is a dark purple bronzy powder which dissolves in water to form a greenish-blue solution.

Blue No. 2, or Indigotine $C_{16}H_8N_2O_5S_2Na_2$, is the sodium salt of the disulfur of indigo,* preferably made from synthetic indigo; it is a blue-brown or reddish-brown powder, which dissolves in water to form a blue solution.

These dyes are listed in the order of their absorption of light in the visible spectrum, beginning with the red end, and proceeding toward the blue.

In addition to the Food, Drug and Cosmetics dyes, there is a list of External Drug and Cosmetics dyes, and another of External Drug and Cosmetics dyes.

The production in 1940, in the United States, was 559,057 pounds of F. D. & C. dyes, valued at \$2.96 a pound; total for the three classes 539,151 pounds, averaging \$0.51 a pound.

New Developments in Dyes. New developments in dyestuffs within the last few years, which are of major importance both as to value and quantity produced, are (1) the Neolan Dyes, (2) Celanese dyes, (3) Polar or I Dyes, (4) Hansa Yellows, (5) the Naphthols, (6) Stable Diazo Salt Rapidogen Dyes, (8) Formaldehyde dyes, and (9) Phthalocyanines.

(1) The Neolan Dyes (Soc. Chem. Ind. in Basel) or Pilatus Dyes are acid azo dyes containing a co-ordinated metal atom in the dye molecule.²¹ It is a well known fact that "Chroming" dyes after they have been applied to the fiber by the addition of chromium salts to the dyeing dyebath increases their stability or fastness to light and washing.

These new dyes are azo dyes made in the usual manner, except that before isolation the solution of the dye is treated with a chromium salt such as chromium formate under reflux or pressure, and the dye is isolated. As a result, the chromium salt of the dye is formed before application to the fiber, eliminating the necessity of a two-step operation in the dyeing. The fastness to light and washing is as good as can be obtained with the older method of dyeing.

Approximately 150,000 lbs. of these dyes were imported into the United States during 1935.

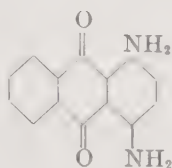
* Formula will be found elsewhere in this chapter.

²¹ British Patent 210,890 (1929); German Patents 369,584; 369,585; 433,148; U. S. Patent 1,706,058; 1,844,396; 1,844,397; 1,844,398; 1,887,602; 1,893,557.

Fabric made from cellulose acetate (Celanese), cannot, as a rule, be dyed with the ordinary cotton or wool dyes. In recent years, with the increase in popular use of Celanese goods, a new group of dyes has been developed particularly for this textile.

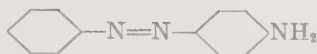
In the production of these, the Celliton (Gen.) Setacyl (Geigy), Celanone (Dupont), Nacelan (National) dyes with various other brands have sold almost 2½ million pounds in 1935. They are made by dispersing water-insoluble organic compounds, usually basic in nature, by means of soaps or sulfonated fatty alcohols, into the colloidal state.²² As colloidal particles these dyes can be applied to cellulose acetate.

Diamino Anthraquinone



violet

Diamino Azo Benzene

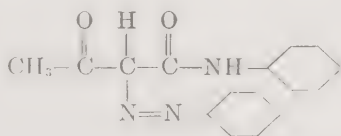


yellow

Typical compounds used in these dyes.

(1) Polar or Milling colors are used on woolen fabrics, such as bathing suits or rugs which are subjected to sunlight and wear. They are dis-azo dyes, the third component being a phenol, which is further condensed with methylol-sulfonyl chloride, markedly increasing the fastness to acids and sea water.²³

(2) Perhaps the most outstanding advance in the pigment field has been the introduction of the Hansa Yellows.²⁴ These colors are clear, bright, fast yellows, in many respects better than the inorganic chrome yellows when used for lacquers or paints. They are azo dyes made by diazotizing amines, or nitro or chloronitroamines, and coupling the diazonium compounds to actoacetanilide or its derivatives.

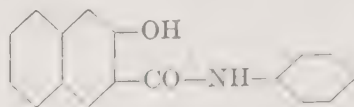


Hansa Yellow

(3) The "Naphthols" are second components for developed dyes, similar to the method of application to Beta Naphthol, but giving more variations.

U. S. Patents 1,448,432; 1,610,916; 1,618,413; 1,618,414.
U. S. Patents 1,067,881; 1,602,776; 1,893,244; British Patent 26,908 (1913).
U. S. Patents 1,059,599; 1,051,565; 1,644,003; 1,082,719.

in shade and better light and washing fastness. The Naphthols are derivatives of Beta Oxy Naphthoic acid.²⁵ For example, Naphthol AS is



Amines, other than aniline, can be condensed with the COOH group of the Beta Oxy Naphthoic Acid in the presence of a dehydrating agent such as PCl_5 , etc., forming other members of this popular series of dye intermediates. In physical appearance they are usually light tan.

They are dissolved in an alkaline solution and are applied or "padded" on the fiber which is then run through a solution of a diazo. Coupling takes place in the α position.

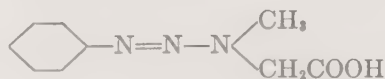
Using various numbers of the Fast Salts (Stable diazo salts), shades of cotton from yellow to black are available. Colors made from the Naphthols are usually insoluble in water and hence are used for pigment and textile printing.

Production and imports of the Naphthols for 1935 totalled more than 6,000,000 lbs.

(6) With the Naphthols came the development of the stabilized azonium salts, the Fast Salts (Gen.),²⁶ solutions of which can be used in place of preparing the diazo solution from the amine in the dyelot. Their manufacture is described in an earlier paragraph. Imports of these Fast Salts for 1935 amounted to 445,695 lbs.

(7) The use of the Naphthols and Fast Salts led further to the development of the Rapidogens and Rapid Fast Colors.

The Rapidogens²⁷ are mixtures of diazamine derivatives of amines. For example,



with Naphthols in molecular proportions. As such they have no color. However, when made into textile printing pastes with suitable thickening agents and applied to the cloth from printing rolls, the color is formed. Subsequent treatment in slightly acid vapors (acetic acid), in a steam chamber.

The Rapid Fast Colors are the nitrosamines of the diazo bodies. They are likewise mixed with molecular proportions of the Naphthols. They, too, are applied to the fabric by printing and the color is developed in the acid chamber.

The principle underlying these types of dyes is that the diazamine or nitroso group can readily be converted to the diazo by the action of acid vapors. Then, before the diazo has had time to decompose, it couples with the Naphthol which was present in the mixture as purchased.

²⁵ U. S. Patents 1,101,111; 1,935,554; 1,819,127; 1,971,409; 1,457,114.

J. Soc. Dyers and Colourists, 40, 218 (1924); 96, 229 (1930).

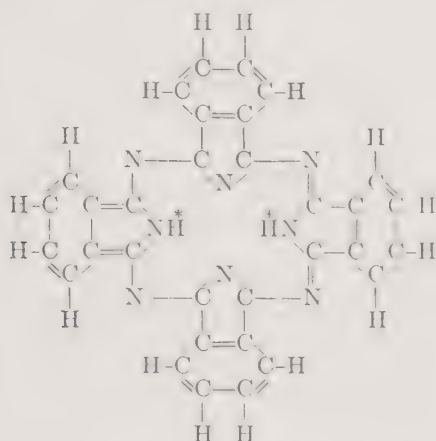
²⁶ U. S. Patents 1,572,715; 1,975,409; German Patent 94,495.

²⁷ U. S. Patents 1,882,560; 1,882,561; 1,882,562; 1,858,623; 1,505,568; 1,505,569.

These dyes compete with the vat dyes because of ease of application and offsets the greater light-fastness of the vat dyes.

b) **Formaldehyde Dyes.** These constitute a new class of direct dyes^{27a} and have very good washing fastness when after-treated with a solution of formaldehyde (10%). They are, for the most part, developed dyes which have been diazotized in the color factory, rather than in the dye house, and have been coupled with resorcinol. The finished color, no longer a developed dye, is sold as a formaldehyde dye for application and after-treatment in the dye house. The resorcinol coupling affects the shade only slightly, and gives a dyestuff of simple application and better fastness, something that the dyer always is looking for.

c) **Phthalo-cyanines.** Phthalo-cyanines are a new class of synthetic pigments and dyes, discovered about 1927, and only recently placed on the commercial market. They are blues and greens, having application in every branch in which colored pigments are used. Many are brilliant in shade and have very good fastness properties. Their basic structure is:



The unmarked hydrogen atoms can be replaced by a number of groups such as halogens,²⁸ sulfonic acids,²⁹ alkoxy,³⁰ aryloxy,³¹ phenyl,³² and many others. The two hydrogen atoms marked with a star can be replaced by metals such as lithium, sodium, magnesium, beryllium, nickel, copper, chromium, etc.³³

Of this new class of compounds the copper phthalo-cyanine, in which an atom of copper is linked by primary valences to the two nitrogens bearing the marked hydrogens and by covalent bonds to the four nitrogens at the corners (in the formula above), is the most popular and is sold as Monastral Blue. Its uses are numerous; for example, it is used in printing inks,

U. S. Patents 1,087,430; 1,878,471; 2,204,230; 2,278,492.
 French Patent 815,088, 7/5/37; British Patent 461,268, 2/15/37;
 Patent 390,149, 3/22/33.
 British Patent 457,796, 12/7/36; British Patent 460,147, 1/18/37.
 British Patent 470,703, 8/16/37.
 British Patent 469,139, 7/20/37; British Patent 470,499, 8/9/37.
 French Patent 811,933, 4/26/37.
 French Patent 322,169, 11/18/29; British Patent 457,526, 11/30/36; British Patent 441,332, 1/13/36;
 Patent 389,842, 3/22/32.

and has superior fastness to older products; artists' color because of brilliance and permanence; paints, lacquer and enamels, where it overcomes poor fastness to alkali of the iron blues and the poor fastness to acids of the ultramarines; water paints; coated textiles; paper; linoleum, because of its fastness to the harsh treatment received in linoleum manufacturing; rubber; plastics, and textile printing.

There are a few solubilized phthalo-cyanines which are finding application in direct and mordant dyeing of cotton and are popular because of brilliance.[†]

Uses and Production. Dyes go to the textile industry, paper industry, leather, foodstuff, fur, pigment, synthetic resins, boot polish, printing and many other industries. A color confined to one industry, for example the woolen industry, would be standardized on wool; on the other hand Nigrosine, Citronine, Resorcine Brown are tested on vegetable-tanned leather.

All dyes and dyestuffs, when isolated, have to be dried, milled and standardized. Drying is done in vacuum shelf driers, which are hot air chambers. Milling is done in a disintegrator, or ball mill. The dyes added are salt, anhydrous sodium sulfate, dextrin, and others.

TABLE 70.—*Production of coal-tar dyes in the United States in 1940.**

	pounds	value
Azo dyes	55,701,277	\$0.62
Stilbene dyes	1,017,379	.66
Pyrazolone dyes	1,218,593	.83
Triphenylmethane and diphenyl-naphthylmethane dyes	4,663,540	1.08
Sulfur dyes	21,560,675	.25
Anthraquinone dyes	3,421,174	1.13
Vat dyes	30,076,000	
of which indigo (20% paste) 11,133,161 at .16.		
Total all dyes	\$127,834,000	.62

* U. S. Tariff Commission Report 148.

For dyes which have a minimum of salt, pressing in a hydraulic press for the removal of the greater part of the adhering water, is coming into general use.

Of interest is also the fact that, at times, a second dye is a by-product and must find an outlet; thus when one ton of Oxyphenine Yellow is made, one ton of Primuline is simultaneously produced.

OTHER PATENTS

German Patent 145,373, on phenylglycine production; U. S. Patent 1,431,300, brilliant indigo; German Patent 237,262, U. S. Patent 1,012,363 and 1,473,887, indigo derivatives; 1,877,800, manufacture of tri-azo dyes, and 1,821,290, of di-azo dyes; 1,848,228, method for making black and gray vat dyes, comprising the condensation of a sulfonated benzanthrone compound with hydroxyl amine, followed by acidification; 1,759,264, manufacture of new sulfur dyes; 2,029,313, production and application of new dyestuffs for cellulose ester and ether by means of an unsulfonated a quinone compound; 2,069,158, dis-azo dyestuffs, insoluble in water, a development for cotton.

[†] Phthalo-cyanines: "A New Class of Synthetic Pigments and Dyes," by M. A. Dallen, *Dyestuff Rptr.*, 28, 603 (1939).

PROBLEMS

Are dyes are manufactured from a bill of materials which lists the pounds of each ingredient, then percentage purity, the molecular weight, the moles used, and molecular equivalents represented. The molecular weight is the theoretical of the moles used and therefore the mol equivalent includes the excess necessary for the reaction to an end, or to exhaust any certain ingredient. Such a list is items for caustic, soda ash, acids, sodium nitrite and other inorganic chemicals. Working in a simpler way: set up the bill of materials which are required to 24 pounds of Direct Blue 2B, assuming that the yields are perfect, and that the quantities will lead to a complete reaction.

With the proper weight of benzidine; make it into diazotized benzidine, then the description in text.

The yield of indigo powder based on the phenyl glycine, let us assume to be 100%. How much indigo blue and from it, indigo white will be obtained from 100 pounds of glycine? How much sodamide will be required, and how much indoxyl acid? The hydroxides used are twice the weight of the potassium glycine; what will be large enough to allow the fusion? The general shape should be as used by the fusion kettle in Chapter 27.

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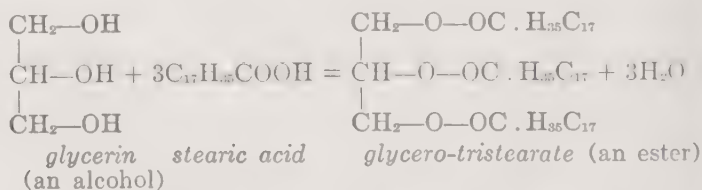
About 100 years ago the French chemist, Chevreul, demonstrated oils and fats such as olive oil and lard were glycerides of fatty acids; on this knowledge as a basis the handling and refining of edible oils and fats was remodeled. Some twenty years ago two French scientists, Sabatier and Senderens, made another important contribution to this field; they transformed oleic acid, an oil, into the solid stearic acid; technologists from every land have constructed a number of devices based on this reaction, so that the "hardening" of edible oils into edible fats is now an established branch of this industry.

Chapter 29

Animal and Vegetable Oils, Fats, and Waxes

The animal and vegetable oils, fats, and waxes are esters of organic acids belonging to the fatty acid¹ series. An ester is formed by the combination of an alcohol and an acid, with the elimination of water. The animal and vegetable oils and fats are glycerin (really, glycerol) esters of a wide variety of fatty acids, in which the glycerin is the alcohol; the waxes are esters of the same kind of acids, but the alcohol is some other one instead of glycerin. The fatty acids belong chiefly to three or four subdivisions: to the saturated series (stearic acid), to the oleic series (which is unsaturated, lacking two hydrogen atoms), or to more unsaturated series lacking four and six hydrogen atoms.

The glycerides of the saturated series melt higher than those of the unsaturated series. A fat is rich in glycerio-stearate, and has some glycerio-oleate admixed; an oil would be rich in glycerio-oleate and poor in glycerio-stearate. Among the glycerides of the saturated acids, a further consideration must be made. One molecule of glycerin requires three molecules of acid to form an ester. If the three acid residues are the same, the fat is rather hard: glycerio-tristearate, called stearin for short, melts at 72° C.; if the acid residues are unlike, the fat has a lower melting point; thus glycerio-distearate-monopalmitate melts at 63° C.



In each oil and fat, a number of different fatty acids occur, sometimes as many as ten, six or more being the rule; this would make the study of the composition of an oil difficult enough. The complications of mixed esters such as glycerio-distearate-monopalmitate increases the difficulty still more; it is therefore not surprising that there are many oils and fats whose composition is still unsettled.

¹ It is because of their presence in fats that these acids have been named fatty acids.

A study of the composition of the oils and fats is based on a knowledge of the constituent fatty acids, a number of which are listed in Table 71, the names of oils and fats in which they occur; the latter are merely tables, for each fatty acid occurs in a large number of oils and fats.²

71. *Fatty acids occurring in the form of esters in oils, fats, and waxes.**

Group A—Saturated Series			
	Melting point of the free acid	Melting point of the simple triglyceride	Chief occurrence
..... $C_8H_{16}O_2$	liquid	liquid	butter fat 4%
..... $C_{10}H_{20}O_2$	31.3° C.	liquid	butter fat, coconut oil
..... $C_{12}H_{24}O_2$	43.6	45	coconut oil 45%
..... $C_{14}H_{28}O_2$	53.8	56.5	butter fat, 22%
..... $C_{16}H_{32}O_2$	62.6	65	palm oil, lard
..... $C_{18}H_{36}O_2$	69.3	72	all fats
..... $C_{24}H_{48}O_2$	74	—	carnauba wax
..... $C_{26}H_{52}O_2$	78	76.5	beeswax
..... $C_{30}H_{60}O_2$	90	89	beeswax
Group B—unsaturated, lacking two hydrogen atoms			
..... $C_{18}H_{34}O_2$	14	liquid	olive oil 70%
..... $C_{22}H_{42}O_2$	33	31	rape oil; fish oil
Group C—unsaturated, lacking four hydrogen atoms			
..... $C_{18}H_{32}O_2$	—	—	cottonseed oil and soya bean oil
Group D—unsaturated, lacking six hydrogen atoms			
..... $C_{18}H_{30}O_2$	—	—	linseed oil 10%
..... $C_{18}H_{30}O_2$	—	—	linseed oil 60%

* "Coconut 45%" means that of the fatty acids present in coconut oil, 45% are lauric acid.
 † Taken mainly from J. Lewkowitsch, "Chemical technology and analysis of oils, fats, and waxes," 3 vols.
 New York and London, Macmillan Co.

The most important vegetable oils are cottonseed, linseed, olive, corn, rapeseed, rape, coconut, palm, and castor. The method of extraction is different for all. The fruit or seed after cleaning by sieving and blowing, and hand selection, is crushed and first cold-pressed for the highest grade, then pressed warm for technical grades; the crushed mass may be extracted further by solvents. In the case of edible oils, the first grade is used for food purposes; the lower grades are used for technical purposes, including the making of soap. In order to be edible an oil must be attractive; it must possess an agreeable flavor (olive oil) and must be free from disagreeable odor. It must be pale in color, usually yellow; it may be without distinctive odor, yet be wholesome and well suited for food. The oils used as food oils in the United States are olive oil, mainly imported, corn oil, cottonseed oil, and cottonseed oil (Wesson oil). The chief use of linseed oil is in varnishes and paints; of rape oil in lubricants, coconut and palm oils are used in soap-making. Vegetable fats are mostly artificial, being made from the oils, such as cottonseed oil, by hydrogenation.

Animal oils and fats are: whale oil and fish oil (both less important than formerly), by hydrogenation of which, fats are formed, which are used in part for soap stock; lard and lard oil, for food; beef, mutton, and

except butyric acid which is characteristic for butter fat.

sheep tallow; fish-liver oils for pharmaceutical purposes; sperm oil, and wax, for lubrication. The method of extraction is essentially a warming that the oil may run off or be pressed out. The best-known waxes are carnauba wax and beeswax.

It will be noted that nothing has been said about distilling; none of the oils and fats can be distilled under atmospheric pressure without at least partly decomposing. They are called fixed oils, in distinction from volatile or odoriferous oils in the following chapter under the general name of essential oils, which are frequently distilled. The oils obtained from petroleum can also be distilled, but they remain well characterized as one group because of their mineral origin. In discussing paints and varnishes, the point of view of the varnish maker is adopted, who thinks of oils as drying, non-drying, or non-drying oils. It is the state of unsaturation indicated by certain fatty acids in Table 71 (groups *C* and *D*), which permits the classification called drying because of oxidation by the air³; it is the same unsaturation which is relieved in another fashion by hydrogenation.

In order to compare successive shipments of the same oil, and in order to detect adulteration, a number of tests are applied, some of which are very old. In the Maumené test, the heat caused by the addition of sulfuric acid is measured. The saponification test records how much potassium hydroxide is consumed in forming the potassium salt of the fatty acid; an adulterant mineral oil would not consume any caustic and would thereby be detected. The iodine value gives a measure of the unsaturation. Specific gravity, refractive index in conjunction with the tests named above, and at least one confirmable by specific tests, permit identification of the oil and estimation of its purity.⁴

The color of oils is lightened by adding fuller's earth, bone charcoal, or precipitated silica or similar finely divided substances, followed by a filter.

The extraction of linseed oil will be described in detail; the procedure for other seed-oils is similar.

LINSEED OIL

Linseed oil is made by pressing warmed flaxseed⁵ which has been previously crushed. Flax is grown in several northwestern states, notably North Dakota, Montana, Minnesota, and South Dakota. Most of it, however, is imported from Argentina, so that linseed oil refineries are located at ocean ports as well as at inland points. The main product is the oil; an important by-product is the press-cake, which forms a valued cattle feed.

The flaxseed is stored in elevators very much as grain is. For the extraction of the oil, the seed is elevated to the top of a five-story building; in subsequent operations it may be fed by gravity. First it passes through screens which remove all coarse admixed matter; then it is fed to a bag blower with numerous small conical bags. These are connected mechanically and automatically with compressed air, which blows out the dirt and small dirt. The clean seed is carried by a screw conveyor to the

³ Compare under varnishes in Chapter 31.

⁴ "Standard methods of chemical analysis," W. W. Scott, New York, D. Van Nostrand; "Chemical technology and analysis of oils, fats, and waxes," J. Leuckowitsch, London, and N. Macmillan Co.; "Vegetable Fats and Oils," G. S. Jameson, New York, Chemical Catalog Co.

⁵ Formerly called linen seed.

er of large storage bins; the crushing rolls are situated under them on the floor. It may be interesting to note that flaxseed is slippery; stepping on a tall bin means that a man will go to the bottom. The seed is small, 3 mm. long, 2 mm. wide, and 1 mm. thick, so that it will escape from the bottom of a farm wagon unless the boards are brought close together.

The crushing device consists of 5 heavy steel rolls placed in a vertical line; the two upper rolls are corrugated. Three rolls are driven, the first, third and fifth; the second and fourth are idle. The speed is 175 rpm. The meal from the bin is fed by gravity to the top roll; by means of small gates, the meal is collected from one roll and fed to the next, making four stages in all. A completely mashed product results, which has lost all loaf shape. The mashed meal passes by gravity to a two-stage, steam-heated kettle provided with slow agitation (30 rpm.). The meal enters the kettle in the center of the first shelf, and passes to the second shelf through circumferential openings. It is drawn from here as required.

The actual pressing is controlled by two men, who operate a battery of presses, three on a side; each press has thirty horizontal shelves. In order to form the meal into a slab-like section, a frame 18 inches wide and 3 feet long is placed on a hair mat of slightly larger size and pushed under a slide at the bottom of the kettle, whose base is just above the working table. The mat is filled by opening the slide; the mat and frame are pulled out and the meal is pressed into shape by an automatic ram. The frame is removed and another similar mat placed over the meal. Three such mats are made each minute.

One of the six presses is always open, in process of being unpacked and at the same time reloaded; the pressed cake from the previous press is removed and in its place a fresh charge is slipped in. Below each shelf a wider metal tray is inserted to collect the oil and guide it through funnels and pipes to the main trough in the floor. It takes 10 seconds to empty and fill a section; the cycle for the press is 60 minutes, 50 minutes actual pressing. The mats lie in horizontal planes; the pressure is applied by a hydraulic ram which rises vertically, from below. The pressure applied is 4000 pounds, and is transmitted by means of heated oil, constantly changed to prevent its turning rancid. Linseed oil is used so that contamination by some foreign oil may be avoided. Each section presses $5\frac{1}{2}$ bushels⁶ of seed per hour (hence also per cycle), or 132 bushels per day, yielding 6.8 barrels⁷ of oil. For the battery of six presses, the production is 40 or 41 barrels. It may be estimated that 20 bushels of seed are required to produce 1 barrel of oil. The number of batteries in a mill varies, but is usually very high. The oil obtained is about 34 per cent of the weight of the seed.

The pressed cake, which resembles a stiff board, is laid on small trucks on a conveyor which brings it to the trimming machine. The edges are cut off because they still contain 30 per cent of oil; these trimmings are fed to the warming kettle. The body of the cake retains 5 to 6 per

⁶ 1 bushel of flaxseed weighs 56 pounds.
⁷ 1 barrel contains 50 U. S. gallons.

cent of oil, which is not removed. The cake is broken into small pieces in a rotating cylinder with projections, and made into a powder in square cage disintegrators⁸ with 52-inch baskets, rotating at extremely high speed. The press-cake powder is shipped in 100-pound bags. So important has this by-product become that the fluctuations in its price⁹ are reflected in the price of linseed oil.

There is also in use a continuous process of extraction, in which warm meal is pressed by a tapering screw; the pressed cake retains about 10 per cent of oil.

In 1939, the production of linseed oil (U. S.) was 534,498.322 tons, valued at 9.1 cents a pound, and that of the cake and meal 519,131 tons, valued at \$32.50 the ton (\$48.30 in 1929).

Refining the Oil. The oil from the press, filtered through duck flannel filter cloths in a plate-and-frame press, is the raw linseed oil for commerce; its color is a yellow-brown.

Large quantities are refined further by gentle heating for definite periods to remove moisture, and by adding fuller's earth followed by filtration through duck, flannel, and thick paper. The heating must be carefully controlled in order to avoid darkening the oil. The effect of the fuller's earth is partly to bleach the oil, partly to assist in the removal of finely suspended matter, called the "foots." For many purposes the oil must be "bodied" in order to give it body, that is in order to raise the viscosity. This is done by heating with steam coils and blowing in air for certain periods. The blowing is usually followed by a filtration.

Although linseed oil will "dry," that is, harden on exposure to air, through oxidation, such drying is too slow for practical purposes. The drying is greatly accelerated by adding small amounts of the oxides of manganese or cobalt,¹⁰ and then heating the oil under reduced pressure. The product is "boiled linseed oil," which dries in a few hours. The oxides act as catalysts of the oxidation.

When fresh, linseed oil is edible. For that purpose it is expressed in this country; this is done on the continent of Europe to some extent.

The special tests for various grades of linseed oil reflect its chief use as a drying oil in paints and varnishes. In addition to the usual tests for color, drying power and sediment content (the foots) are observed.

VEGETABLE OILS

Olive Oil. Because of its flavor, olive oil is the most highly prized of the edible oils. The olive tree is cultivated in Italy, southern France (Provence), Spain, Algeria, Tunis, and southern California. In general, the fruit is picked just before it is ripe; its content of oil varies from 35 to 40 per cent. The pressing for the highest grade is done cold, sometimes with the stone, other times after the stone has been removed. The fruit is packed in muslin bags and placed in a cylindrical cage surrounded by a sheet

⁸ Chapter 44.

⁹ The press-cake meal sells normally for \$40 to \$45 a ton.

¹⁰ Three-tenths per cent lead oxide, 0.1 per cent manganese dioxide, or 0.05 per cent cobalt oxide have the same accelerating power; a mixture of any two is still better. Iron oxide is also effective, but it is not favored because it discolors the oil.

ope to catch the squirting oil. A heavy cylinder is applied from above, gradually increasing force applied by means of a hand-operated screw. oil collects in the floor trough. The color is pale yellow.

The pulp is mixed with cold water and pressed again, best with hydraulic pressure, and a second quality of edible oil is obtained. Made up with water, still another quality of edible oil is secured. Finally the pulp is extracted with carbon disulfide, which gives a dark product suitable for making. There is a difference in composition in the various grades. Free fatty acids, resulting from hydrolysis, are less than 1 per cent in highest grade, 5 per cent in the next grade, and as high as 20 per cent in the lowest technical grade.

olive oil contains mainly the glyceride of oleic acid, an unsaturated acid. It is a non-drying oil.

Peanut Oil. This oil is a very acceptable substitute for olive oil. It is obtained by pressing the peanut, or earth-nut, and is called in Europe *Arachis oil* from the name of the plant, *Arachis hypogaea*. The seeds or nuts contain 43 to 46 per cent of oil. The shells and skins are removed, the seeds are ground in squirrel-cage disintegrators, and cold-pressed first, when 40 per cent of the oil is obtained. This grade is used for salad oil, and has a pleasant nutty flavor. Two more expressions at higher temperature furnish technical grades.

Corn Oil. When starch is made from corn (maize) there is obtained as a by-product the kernel, which, on pressing in the same way as flaxseed, yields an oil, and a press-cake which is a cattle food. The corn seed contains 50 per cent of oil; when it is pressed cold, a pale yellow product is obtained having a slight odor. This is removed by refining, and the oil is placed on the market as a salad oil, in part under the name of Mazola in the United States. The lower grades are used for soap-making, and to a limited extent in paints and varnishes.

Palm Oil. The best grades of palm oil are edible. The fresh fruit is heated slightly warm, and a pale yellow, butter-like material is obtained; consumption is limited to the natives of West Africa,¹¹ where the palm *Elaeis guineensis* grows. The greater part of the oil is obtained by allowing the fruit to ferment in holes in the ground, then either pressing the softened fruit or boiling it in water and collecting the oil which rises. The oil so obtained is suitable only for technical purposes, largely soap-making. Several other varieties of palms are cultivated in South America, and worked in the same manner.

The palm kernels are collected separately and yield a soft fat of different composition from palm oil. The kernels are generally imported to Europe and the United States and utilized with modern working methods.

Cottonseed Oil. The oil produced in the greatest quantity in the United States is cottonseed oil. Its production is twice as great as that of linseed, and in turn is five times the combined imported and home-produced olive oil. Table 72 indicates the relative importance of a number of the important oils.

except for a small quantity placed in some margarines for color.

TABLE 72.—*Production, imports, exports and consumption of vegetable oil in the United States for 1939.**

	Production	Imports	Exports	Consumption
Cottonseed oil	1,389,791,503	711,800	3,879,739	1,392,200
Linseed oil	561,507,734	48,670	2,566,060	344,900
Coconut oil	273,271,444	336,795,877	15,263,365	587,600
Olive oil, edible	6,852,887	62,866,228	436,581	3,900
Palm oil	none	286,416,373	815,837	263,200
Palm kernel oil	none	325,226	13,870,721	84,000
Babassu oil	71,378,600	no record	no record	67,200
Corn oil	150,555,463	13,964,861	179,548	150,200
Castor oil	75,605,782	no record	no record	41,000
Peanut oil	73,138,000	3,779,415	no record	76,800
Soybean oil	457,549,510	4,125,526	12,110,936	395,900
Rapeseed oil (colza)....	none	8,971,815	no record	6,500
Tung oil	none	78,717,634	5,911,261	90,700
Sesame oil	small	no record	no record	2,200

* Based on figures from the Bureau of the Census, Department of Commerce. The figures are in pounds, for the crude oil.

The cottonseed contains 20 per cent of oil; each pound of cotton seed contains two pounds of seeds. The shell is cut by rotary knives and separated from the seed proper in a wire gauze basket which rotates, letting the seeds fall and retaining the hulls. The decorticated seeds are crushed and pressed, and crude cottonseed oil red or brown in color is obtained. It is refined by warming it with a solution of caustic soda which removes much of the impurities and neutralizes the free fatty acids. The caustic solution forming the emulsion layer is run off, and the remaining oil washed. On standing in the open, the solid glycerides separate, and are removed by filtering under pressure. The oil may be bleached further by adding fuller's earth and filtering; special grades are prepared in this way. It is used to some extent as an oil, but finds constantly greater extent for hydrogenation, which gives cooking fats. It finds considerable use in making butter substitutes. Formerly it was largely used for making hard soap; to some extent soybean oil has displaced it. Cottonseed oil is a semi-drying oil.

There were produced in 1939, 1,409,413,537 pounds of cottonseed oil, valued at 6.2 cents a pound; in 1933, the price had been 3.23 cents a pound. The cake and meal produced in 1939 amounted to 2,023,341 pounds at \$23.57 a ton (\$14.04 in 1933). Linters were 1,113,312 bales at \$11 a bale (\$8 in 1933).

Coconut Oil. The cocoa palm grows in South America, India, Ceylon, China, in the Philippine Islands, and other countries. The fruit is imported in the dried condition under the name of copra. The oil is expressed at 60° C., and is edible, either as such or mixed in margarines. The cake is a cattle food.

The production of coconut oil is next to that of linseed oil (the United States).

Soybean Oil. The soybean contains 20 per cent of oil; it is produced chiefly in Manchuria, where the oil is also extracted. The method is to steam the bean and to press it warm; the yield is about 10 per cent. Soybean oil is a semi-drying oil, and is used in varnish making, also for soap. Soybean has been raised for forage in the United States, but not in any quantity for oil production until recent years.

Castor Oil. Castor oil is obtained from the seed of the castor plant, *Ricinus communis*, which grows in the West Indies, India, and other tropical countries. The seed contains 45 to 50 per cent of oil. The best grade, cold-pressed oil, is widely used as a mild cathartic. Other grades are edible as lubricants, mixed with mineral lubricating oil. Castor oil is a drying oil; it is a plasticizer for Celluloid and for lacquers.

Sulfonated Castor Oil or Turkey Red oil is sulfonated castor oil. Concentrated sulfuric acid is mixed with castor oil at temperatures not exceeding 100°C. After some time, a small amount of water is added, and the dilute acid, which separates as a lower layer, run off. The oil is washed with a sodium sulfate solution. Ammonia is added in amount insufficient to neutralize the remaining acid, but sufficient so that the oil gives a clear emulsion with water. The soluble oil is used extensively in the preparation of dyes and fibers for dyes (Chapter 26).

Rape Oil. Rape oil, *Brassica campestris*, is cultivated in Europe; seeds are also imported from India, and oil from Japan. The seed has 40 to 45 per cent of oil; the treatment is similar to that of flaxseed, and the press-cake is a cattle food. Rape oil has non-gumming properties, and finds extensive use as a mixed lubricant, with mineral oil.

Sesame Oil. Sesame oil is of some importance in Europe. The sesamum is imported from China and India. The best grades are edible, either as salad oil or in margarine; the lower qualities serve for soap making.

Chinawood Oil, or Tung Oil. The seeds (*Aleurites cordata*) in a nut the size of a small orange contain 53 per cent of tung oil. When it is pressed by the ordinary methods, 40 per cent of the oil is expressed. In China, this oil is used by the river men to impregnate the wood of boats and rafts in order to make them waterproof, hence the name, "China wood oil." This oil has had a tremendous importance in varnish making; it dries in one-third the time which linseed oil requires, and has other valuable properties of varnish, for example, excellent resistance to sunlight. Chinawood oil consists chiefly of the glyceride of elaeostearic acid. Within the past fifteen years trees have been planted in the United States, chiefly in Florida. An experimental farm has been established in Mississippi.

Dehydrated castor oil and oiticica oil are mentioned in Chapter 31.

ANIMAL OILS AND FATS

Whale Oil. Whale oil formerly was an important source of oil for burning; the advent of petroleum products has relegated it to an unimportant position. The annual world's production of whale oil is about the amount of cod liver oil imported into the United States. The seats of the whaling industry are Norway, Iceland, and the American Pacific coast.¹²

A large whale yields between 100 and 150 barrels of oil; the blubber or baleen is rendered either on board the boat or in the home port. The fat is rendered fine and rendered by heating first by itself, then with water; cer-

¹² There are 4 shore stations, each handling whales caught within a radius of 150 miles: Moss Landing, in California; Bay City, Washington; Akutan, Alaska. Production in 1930, 10 million barrels. The most important whaling grounds of the world today are in the Antarctic, particularly in the Ross Sea. (From the Bureau of Fisheries, Department of Commerce, Washington, D. C., and the Census.)

tain parts of the carcass may also be digested for oil. The uses are leather dressing, burning oil, soap, and, mixed with mineral oil, for a paint. Whale oil is also hydrogenated to a fat.

Fish Oil. Fish oil is obtained by boiling either the whole fish or selected parts in water and collecting the oil which rises. The menhaden, herring, and certain salmon are used in large numbers for this purpose, and other fish in smaller numbers. The residue in the rendering pots is sold and sold for fertilizer. Fish oil is used in cheap paints to replace part of the linseed oil and for other minor purposes. The oil may be hydrogenated to a fat, at the same time losing its unpleasant odor; such fats are suitable for soap making (1935 production about 55 million pounds).

Cod-liver Oil. The cods are brought alive to the home station in steam trawlers, opened, and the fresh livers heated in steam-jacketed kettles. The first oil is prized for its vitamin A and D content, and is used for medicinal purposes. On continued heating a second grade of oil is obtained, which is used in fine poultry raising. Livers which are brought in partly decomposed are rendered for an oil used in the dressing of leather. The production was 2,458,626 pounds, the consumption 18,711,586 pounds. The exports were 50,027,055 pounds. The livers of many other fish are similarly treated, the most important being halibut, tuna, and shark.

Lard and Lard Oil. The fat of the pig is rendered by heating it in water in closed, cast-iron vessels under pressure and provided with an outlet for the release of overpressure caused by the formation of gases. After digesting, the liquid is run off; by cooling it moderately, a division into a liquid part, the lard oil, and into a solid part, the lard proper, is made. The lard oil is divided into lard oil proper, and oleo oil; both serve a variety of purposes. In 1939, there were produced in the United States 1,410,611,189 pounds of lard, 22,444,537 pounds of lard oil, and 75,860 pounds of oleo oil, a grade of lard oil; there were exported 277,271,534 pounds of lard.

The operation of rendering has recently been improved and accelerated. In the circulating rendering process of Wurster and Sanger, Chicago, several desirable ends have been reached: (1) Quick heating, which reduces the time factor and the objectionable yellow color; (2) low temperature, avoiding scorching; (3) larger capacity for a given time period.

The equipment for this process includes a tubular heating element consisting of vertical tubes through which the ground material passes, flash chamber, a circulating pump, separator, and a vacuum pump. The tubes are heated by exhaust steam, under 5 pounds pressure. The material is drawn into the base of the tubes by a centrifugal pump of the non-clogging type. The material is returned at a point just above the tubes. The heater is surmounted by a flash chamber in which the gases evolved are collected before they pass to a separator where the droplets of entrained fat are recovered, to be returned to the main drum. From the separator, the gases go to the steam ejector which maintains a low pressure on the system. After the material is completely melted, it is discharged into a settling tank, from which the fat is drawn off. The sediment, called cracklings, is run to a filter press.

With a heating surface of 1000 square feet, a charge of eight to

ered in two hours. Compared with the older type of jacketed melters, high pressure steam (50 pounds), it is found that the new rendering process equipment works four times as fast, besides producing a paler product. Several other details are exhibited in Figure 180.

Tallow. By tallow is usually meant beef tallow, which is rendered in the same way as lard. There is also a mutton tallow, a sheep tallow, and others. Their chief use is for soap-making.¹³

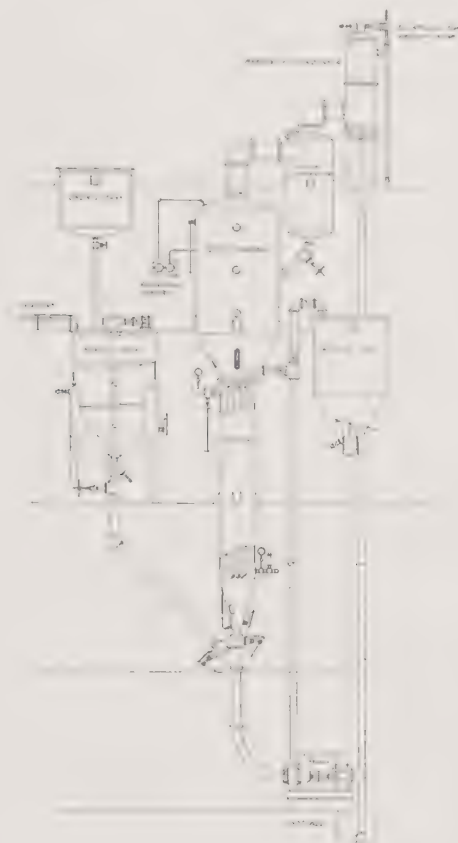


FIGURE 180.—A circulating rendering plant. (Courtesy of Wurster and Sanger, Inc., Chicago.)

Butter. The cream in cow's milk isolated in a centrifugal separator is in small globules of fat, which coalesce on churning; the lump so obtained, after addition of salt (in the U. S.), is table butter; it is about 83 per cent butter fat, the rest water and salt.

WAXES

Sperm Oil. Sperm oil is obtained principally from the content of a cavity in the head of the cachalot or sperm-whale. When the oil is cooled it yields a solid wax, the spermaceti, used in pharmacy and in candlemaking. The oil under the name of sperm oil is valued as a lubricant for light-speed machinery; like rape oil, it has no gumming tendency. The

Lard m.p. 36° to 40° C.; tallow, 40° to 45° C.

chief ester in spermaceti is cetyl palmitate, $C_{16}H_{33}O \cdot OC \cdot C_{15}H_{31}$. Cetyl alcohol is a monohydric alcohol $C_{16}H_{33}OH$. Spermin oil similarly contains trihydric alcohols combined with fatty acids different from glycerin (annual production about 1 million pounds).

Carnauba Wax. Carnauba wax is found on the leaves of a palm in Brazil, the *copernicia cerifera*. The leaves are gathered and rubbed to dislodge the coating: it is purified by melting, decanting from the dregs, and cooling. It has a high melting point, $105^{\circ}C$., and is used in the varnish industry and in furniture and shoe polishes and in carbon paper coating. It is the hardest wax known.

Beeswax. Beeswax is obtained from the honeycomb of the common bee; it is purified by washing and bleaching. Industrially, it is of small importance.¹⁴

HYDROGENATION

The hydrogenation of oils with the aid of a catalyst is an established industry. The reaction is used mainly for the hardening of vegetable oils to edible solids, particularly, in the United States, for the hydrogenation of cottonseed oil; but it has been extended considerably, for instance, to the hardening of fish oils, which are then made into soaps and stearic acid substitutes.

The commercial procedure is to suspend finely divided nickel in the oil, heated to 250° to $300^{\circ}F$. (121° to $149^{\circ}C$.) and blow in hydrogen gas. Nickel gauze may be used instead of the powder. Agitation of the oil by rotating arms is customary. The nickel is used in amounts of 0.5 to 1 per cent of the weight of the oil. It may be introduced in the form of its oxide, which is soon reduced to the metal by the gas; but previous reduction in a separate vessel is the better procedure, for among other reasons the oxide may be filtered out almost completely after the reaction, while in the case of nickel when the oxide is used, an appreciable amount remains dissolved in the oil, presumably in the form of a soap. Palladium is a far more effective catalyst; 1 part in 100,000 parts of oil is sufficient, and the reaction proceeds at a lower temperature, and in less time. In spite of these advantages palladium is rarely used, because of its high cost.

The hydrogen gas must be pure,¹⁵ and should be introduced at the slow rate at which it is absorbed.

Raney nickel is a well-known and much-favored form of nickel catalyst, made by treating a pulverized alloy of nickel and silicon (40 to 40, or 50 to 50), with caustic solution.^{15a}

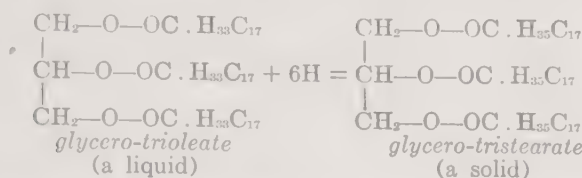
Any glyceride which is unsaturated may be hydrogenated. For example, glyceryl trioleate, a liquid, is thus changed to glyceryl tristearate, a solid. The hydrogenation may be continued until all the unsaturation has been relieved; the result is a fat which melts too high, for an edible fat should melt below the body temperature. It has become the practice to hydrogenate only far enough to form a fat of the desired melting point, and

¹⁴ Some other vegetable waxes which are of interest to the perfume maker will be found discussed in Chapter 30.

¹⁵ Chapter 19.

^{15a} U. S. Patents 1,563,587; 1,628,190; 1,915,473.

mix the harder product with fresh oil. The progress of the reaction is followed by samples drawn off at intervals.



When the catalyst is "supported," the support is generally diatomaceous earth. Its preparation consists of adding 15 to 20 per cent of the earth to nickel sulfate solution, stirring, and at the same time precipitating the nickel as oxide by a solution of sodium carbonate. The precipitate is washed, filtered dry, and reduced with hydrogen at as low a temperature as possible (300° to 400° C. or 572° to 752° F.). The finished catalyst should contain 20 to 25 per cent Ni. As soon as it leaves the reducing furnace, the nickel catalyst is placed under oil, to preserve its activity.

The "wet" reduction, illustrated in Figure 181, which shows a complete hydrogenating plant, is still better, and consists of suspending nickel carbonate or nickel formate in the oil, heating and agitating, with simultaneous entry of hydrogen. The temperature is 225° to 250° C. (427° to 482° F.).

The catalyst is then pumped to the converter, in which the charge of oil has been brought to reaction temperature by a steam coil. The reaction temperature depends upon the purity of the hydrogen and the activity of the catalyst. It is usually 120° to 176° C. (250° to 350° F.). Hydrogen is admitted through a perforated pipe at the bottom of the converter, so that numerous fine streams are formed. The unused gas at the top of the converter is pumped away and recirculated through the bottom pipe, with fresh oil, and a part of the liquid is pumped from the bottom of the converter through a spray coil at the top of the converter. A high-speed propeller at the bottom of the converter agitates the oil. The necessary intimate mixing necessary for rapid reaction is thus insured.

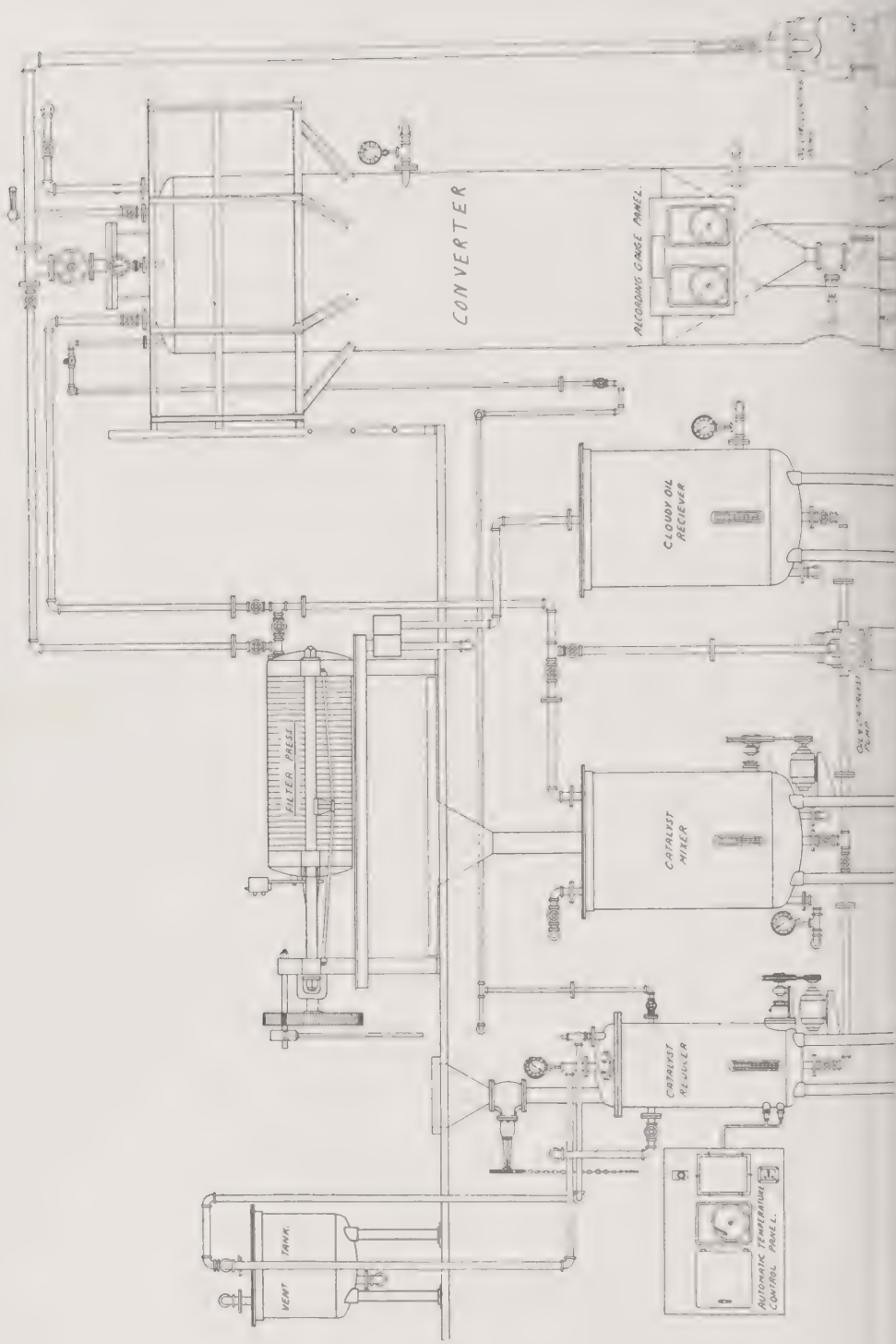
The hydrogenating reaction is exothermic for all oils, so that after it is started, a part of the oil must be cooled by passing it through an outside cooling coil.

After the reduction has proceeded to the desired point (conveniently followed with a refractometer), the charge is cooled somewhat, filter-pressed, and in some cases deodorized by passing carbon dioxide into the melted oil, heated to 130° C. (266° F.), for an hour, or by some other method. On cooling, it is now a soft solid, a semi-synthetic fat. The catalyst is mixed with oil and used over again.

If completely hydrogenated, cottonseed oil would melt at 62° C. (144° F.); for making the edible fat, hydrogenation is stopped when a melting point of 34° to 35° C. (93° to 95° F.) has been reached.

A continuous method for hydrogenation has been devised by Bolton and Co.¹⁶ in which the catalyst consists of nickel turnings or wire held in a

¹⁶Recent advances in the hydrogenation of oils," E. R. Bolton, *J. Soc. Chem. Ind.*, 46, 444T (1927).



sket which nearly fills the hydrogenator. The warmed oil enters at the top, the hydrogen gas at the bottom, with recirculation. Hydrogenation with the corresponding hardening take place, and its degree may be controlled by altering the rate of oil flow; feeding slowly will give high hardening, feeding fast will give only slight hardening. Among other advantages of this process is the one of short period of heating, which gives a pale color.

The hydrogenated oils produced in the United States in 1939 were mainly edible oils, and amounted to 786,890,442 pounds.

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Formerly the material used by the perfume maker were entirely natural products; these are now supplemented by a number of synthetic products. The preparation of the synthetic substances and improved methods of extraction of natural substances are the contributions of chemistry to the perfume industry. The work of the perfume maker, which consists of the proper blending of odoriferous substances, requires artistic as well as scientific knowledge.

Chapter 30*

Essential Oils, Perfume Sundries, Flavors, Pharmaceuticals

Perfumes are made from essential oils, the odoriferous principles of a number of plants. Usually a number of oils are blended together, in a solution, and a fixative is added in order to render more lasting the perfume which otherwise would be fugitive. A perfume may therefore be said to consist of three parts: the odoriferous part, the fixative part, and the diluent.

TABLE 73.—*Essential oils with place of origin.*

Oil lavender fleur	from the flower, hence "flower oil"	France
Oil ylang ylang Bourbon†	from the flower	Réunion
Oil of rose	" " "	Bulgaria and France
Oil of patchouli	from the leaf	Singapore
Oil eucalyptus	" " "	Spain and Australia
Oil geranium Bourbon	from the herb	Bourbon Islands, Algeria
Oil rosemary	" " "	France
Oil thyme red	" " "	Spain and France
Oil bergamot	from the fruit	Spain, France and Syria
Oil orange and oil lemon	" " "	So. Italy
		So. Italy, California, Indies and Africa
Oil fennel	from the seed	Middle Europe
Oil anise	" " "	China, Spain, Russia
Oil caraway	" " "	Europe, North Africa
Oil bois de rose	from the wood	French Guiana and Brazil
Oil guaiac wood	" " "	" " "
Oil vetivert	from the root	Bourbon Island
Oil of orris (a solid)	" " "	No. Italy and So. France
Oil olibanum	from the gum	Arabia, Levant
Oil cinnamon Ceylon	from the bark	Ceylon
Oil citronelle Java	from the grass	Java
Oil palmarosa Turkey	" " "	Turkey

† Old name for the French possession Réunion.

The function of the diluent, practically always ethyl alcohol, is to concentrate the blended oils to an odor strength similar to that of the flower. The number of typical fixatives is small; the numbers of essential oils, very large. The synthetic substances are usually pure chemical substances, whereas the essential oils are natural mixtures. Some syn-

* In collaboration with Mr. Earl Booth, chemist-perfumer, Larkin Company, Buffalo, N. Y.

artificial reproductions of natural substances, others give entirely new essential oils are obtained not only from the flower, but also from the leaves, roots, and seeds of plants, and from the roots and barks of trees. § 73 gives a number of examples, with the places of origin.

Essential oils are used not only for perfumes proper, but also for perfumed soaps; for that purpose they must be lower in cost. As a rule an essential oil costing less than \$5 a pound may be used for soaps. For perfumes proper, there is no price limit, except that for the less expensive ones, the cheaper raw materials must be used; many of these are synthetics. Examples of synthetics follow:

<i>Class</i>	<i>Samples</i>
acids	Benzoic acid, Phenyl acetic acid (solids)
alcohols	Linalool, Terpineol (liquids)
aldehydes	Benzaldehyde, Phenyl acetic aldehyde (liquids)
esters	Amyl salicylate, Benzyl acetate (liquids)
ether	Di-phenyl oxide (solid)
ketone	Ionone α and β (liquids)

Among the synthetics, certain ones are made from benzene, toluene, naphthalene, or other coal-tar products; thus benzoic acid and benzaldehyde from benzene, diphenyl oxide from phenol. These may be said to be true synthetics. Others are semi-synthetic only, for they are made from a natural product; thus ionone is made from citral, which is isolated from lemongrass oil. If a constituent of a natural oil is isolated, by distillation or extraction, and used as such, it is called an isolate; thus geraniol is an isolate from citronella oil.

A number of essential oils are used as flavors as well as perfumes, for example the oils of lemon, bergamot, and orange (peel). Vanillin, oil of clove, and coriander oil are used both for flavoring and for perfumes. Another example is oil of peppermint which has a further interest in that when cooling it,¹ large crystals of menthol separate; this is much used in chewing pastes as a flavor, and also as a pharmaceutical. Formerly the pharmaceuticals were chiefly plant extracts; now they include a large group of manufactured chemicals, of constantly increasing number and importance.

ESSENTIAL OILS

Essential oils are obtained by extraction with volatile solvents, by steam distillation, by expression, and by enfleurage.

Extraction by means of volatile solvents is of wide application, and is the most important method for fine oils. The practice in southern France for the extraction of rose may serve as example. The rose cultivated in Provence is *Rosa centifolia*, a pink rose. The petals are placed on trays in copious quantities and percolated with low-boiling petroleum ether; the waxes and resins are dissolved as well as the oil. The solvent is removed in stills under reduced pressure so that only very gentle heat is required, and there remains a semi-solid residue, called concrete, and containing about half its weight of oil. The rose concrete is next dissolved in warm alcohol, and this

Japanese peppermint oil is rich in menthol.

solution is cooled. The waxes separate and may be removed by filtration. The filtrate is placed in small copper stills, the alcohol removed by distillation, and there is left the pure oil of rose, called rose absolute No. 1. The waxes may be washed again, giving a solution called rose extract. The amount of oil in one rose blossom is very small; to produce 1 ounce of absolute, some 60,000 blossoms are required. By weight the yield is 0.1 per cent. The price is about \$10 an ounce, and this is not too high considering the labor involved in growing and preparing the many blossoms required.

The best known concretes are rose, jasmin, tuberose, orange flower, (a small yellow flower), and lavender; the corresponding absolute oils are made by alcoholic extraction. Concrete violette de Parme, formerly so well known, is now extinct in perfumery. Some perfumers prefer to buy the concrete, and make their own alcoholic extracts of the same without reducing it to the absolute form.

The most expensive of the absolute oils is violet, which brings \$30 an ounce if free from any addition. Violette de Parme is almost too dear for the odor value received when compared with modern Ionones, and for this reason, violet perfumes are made chiefly from methyl ionone, a synthetic.

In order to obtain the oil by distillation, the blossom, herb, or chervil root is placed with water in a still with goose-neck, and heated by a steam coil, or steam jacket, or by live steam introduced below the false bottom, which the material rests. For peppermint, which is a good example, the distillate may be cooled in a condenser made of ordinary conductor pipes, such as are used for rain drainage on dwellings; the cooling is by cold water. The first home-made installation has been replaced in most cases by modern equipment. In the receiver, two layers form, the oil being the upper layer, the water layer is wasted, in this case. In the case of rose blossoms, however, the water retains a certain amount of oil in solution, and is then fully preserved and sold as such, for the demand is considerable. The proportion of rose water to oil may be reduced if desired by returning the still so that new water need not be introduced; in such cases a steam jacket would be the source of heat. Bulgarian otto of rose is a distilled product and is the ordinary otto of commerce; real French otto of rose is rarely seen at the present time because the production cost is less in Bulgaria. The blossoms used in Bulgaria are the *Rosa Damascena*, a rose.

There may be a combination of odors in the distillation itself with certain results; thus geranium (the whole plant) may be distilled by itself, giving geranium oil; or rose petals may be added to geranium oil made the previous fall, and the two distilled together, with the production of oil of geranium roses, possessing a superior odor.

Steam distillation is suitable for the production of the oil because the essential oils are either insoluble, or very slightly soluble in water. The industry is seasonal, so that every year the raiser of peppermint or geranium mint uses the still for two or three weeks; a simple installation is economically correct. For many oils, the dried leaves or roots, produced in the place, may be shipped to a center for extraction, and in that way raised

ded for constant operation; in such centers very elaborate machinery is provided. The most important of these centers is Grasse, near Nice, surrounded by flower-producing areas, and in addition receives imported materials such as patchouli leaves and vetiver roots from India, and orris from Italy (Florence). The important products at Grasse are neroli from the bitter orange blossom, jasmin, verbenas, narcissus, jonquil, orris, rose, cassia, and violet; these are not excelled by products produced elsewhere. French lavender oil is the main lavender oil; English lavender oil was of importance, but is now practically extinct. Material reaching the market labeled English lavender oil is usually a blend of French and English. Steam distillation is the chief method of producing oils, thus, orange, bergamot, verbenas, orris and lavender; the second method is extraction by the use of solvents, already mentioned.

Other products of steam distillation are oil of cloves, cinnamon oil from bark (very little), coriander from the crushed seed, guaiac from the bark, found in India; oil bois de rose, which has no relation to the rose or its oil but is obtained from a laurel in French Guiana; oil of vetiver, citronella oil from Java (best) and Ceylon; and geranium oils.

The peel of the orange, the bergamot, a small citrus fruit on the order of lime, and the lemon, are pressed, both by hand and by machinery, in order to obtain the oil they contain; there is also a distilled oil of these fruits of inferior value. The oils have a high content of terpenes and steropton (steropton is the name given to any wax which separates from oil on standing). In order to concentrate the citral, the characteristic terpenous part in the case of lemon oil, the terpenes are removed by distillation in a steam-jacketed vacuum still (not by directly introduced steam), and the residual oil is then terpeneless oil of lemon, or orange. The terpeneless oil serves as diluent for inferior quality or synthetic oils. It is because of the high terpene content (about two-thirds) of these oils that they change on standing. Presumably the terpenes polymerize, gaining weight, until the odor of the citral is overbalanced; the spoiled oil is termed rancid. Chemically pure citral is mentioned in the next division.

In the enfleurage by the cold process, the flower or the separate petals are pressed against warm fat, a fine grade of benzoinated lard, spread on glass plates 1 foot wide by 2 feet long, fitted with wooden frames. Both sides of the glass are greased; petals are placed on the upper side only, and the plates are piled on one another, so that the lower side touches the petals on the upper side of the frame below. After a day the petals are removed by hand, the plates are brushed, fresh petals spread on, and this repeated until the lard has absorbed the maximum amount of oil it can absorb. The lard is then scraped into pans and preserved in cooled cellars; at this stage the product is called pomade, formerly used as such. From the pomade, the absolute oil is obtained by extraction with alcohol, followed by a distillation to remove the alcohol, and in order to distinguish such absolute from that obtained by the solvent method, it is called "absolute pomade," thus Jasmin Absolute Pomade. This process is used less than formerly; much labor is required, and the fat tends to turn rancid; efforts to substitute soft paraffins have not been successful, because their absorption power is low.

A modification of enfleurage is to macerate the rose blossoms with warm oil, filter from the blossoms, and cool; the resulting pomade may be extracted from the oil by alcohol. The alcohol is recovered. Rose and orange blossom pomades are made by the hot process, jasmin and tuberose pomades by the cold enfleurage process.

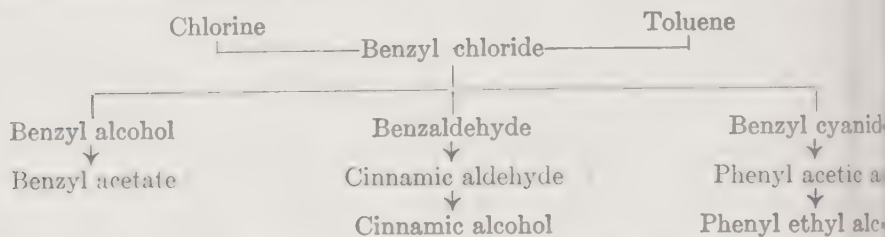
TABLE 74.—*Approximate annual production of essential oils.*

Otto of Rose	3600 kilos to 1000 kilos (varying according to season)
Oil Lemon It.	1,200,000 lbs.
Oil Orange It.	250,000 lbs.
Oil Orange Sp.	70,000 lbs.
Oil Bergamot	400,000 lbs.
Oil Aspic Lavender Sp.	220,000 lbs.
Oil Rosemary Sp.	330,000 lbs.
Oil Lavender Fr.	300,000 lbs.

SYNTHETICS, SEMI-SYNTHETICS, AND ISOLATES

Benzaldehyde is made by chlorinating toluene, and boiling with caustic soda; its odor is similar to that of bitter almond oil. Nitrobenzene² is called oil of mirbane, and has a penetrating odor; its use is chiefly for soaps and shoe polish. Dimethyl hydroquinone is a white solid, valuable for synthetic narcissus perfumes. Cinnamic aldehyde has been sold under the name of Cassia oil redistilled; it may indeed be isolated from cassia, but like all other substances in this paragraph, it is made synthetically with great care and at low cost.

The chemical relation between a number of synthetics is shown in the following diagram:

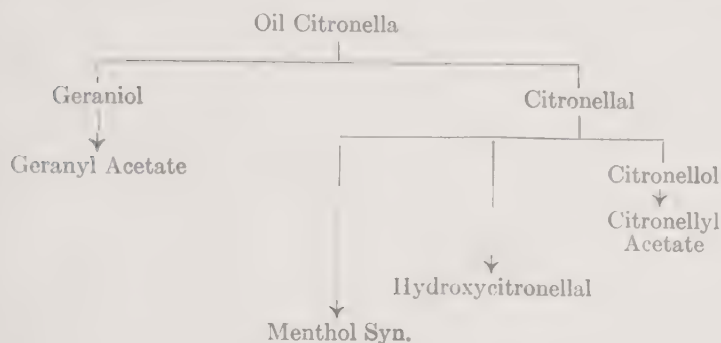


Vanillin^{2a} is a semi-synthetic; it is made (1) from iso-eugenol, which itself is made from eugenol, an isolate from oil of cloves or cinnamon oil; (2) from guaiacol fractionated from the phenols in coal-tar; (3) from wood pulp. Vanillin is a white solid, and in this form is used by the perfumer, rather than in the form of the extract from the vanilla bean. The odor of vanillin is delicate; vanillin forms part of a surprisingly large number of perfume formulas. Piperonal^{2b} is a solid aldehyde, sold under the name of heliotropin. Coumarin^{2c} is made synthetically, although it occurs naturally, for instance in tonka beans; it is a white solid prepared from salicyl aldehyde; its odor is sharper and more penetrating than that of vanilla. The most remarkable of the semi-synthetics is the ionones, ketone isomers differing only in the position of a double bond (unsaturation); α -ionone is about \$8 a pound, β -ionone about \$6. The ionones are made by condensing citral with acetone, and boiling with dilute sodium hydroxide.

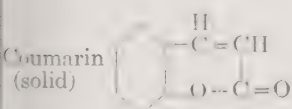
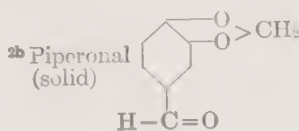
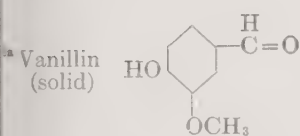
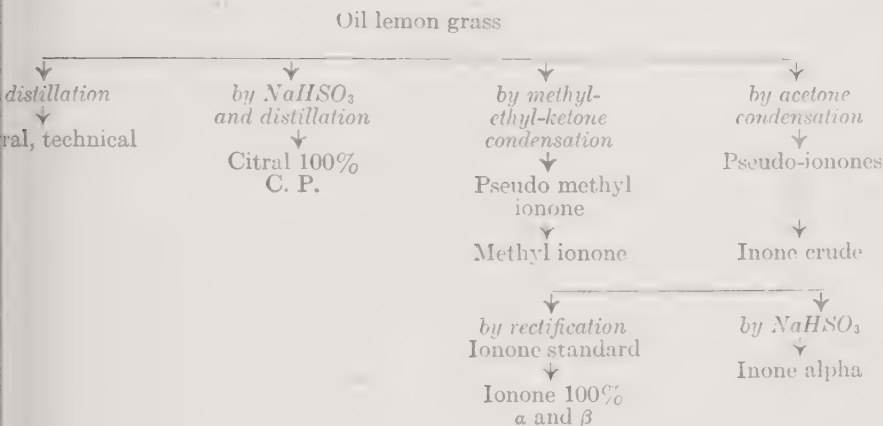
² Chapter 27.

Citral is a liquid of formula $(\text{CH}_3)_2 \cdot \text{C} : \text{CH} \cdot \text{CH}_2 \cdot \text{CH} \cdot \text{C}(\text{CH}_3) \cdot \text{CHO}$, and is isolated from lemon-grass oil by forming the sodium bisulfite addition compound; pure citral is \$2 a pound. The two isomeric citrals are separated by their sodium bisulfite compounds, which differ in solubility (the α -ionone compound is less soluble). Methyl ionone with suitable admixtures produces a true violet odor. All the substances in this graph except coumarin are semi-synthetics.

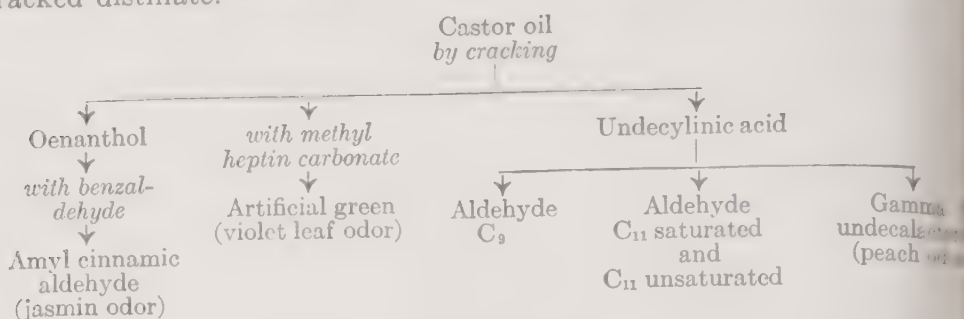
Geraniol is an important substance, an example of an isolate, it is obtained from palmarosa oil or citronella oil, and serves to imitate the rose



From lemon-grass oil, a number of valuable semi-synthetics are obtained:



A new method of preparing a number of semi-synthetics for their color and flavor is the cracking of castor oil, with subsequent treatment of the cracked distillate.³



PERFUME SUNDRIES—FIXATIVES—RESIN OILS

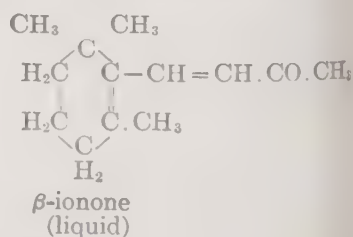
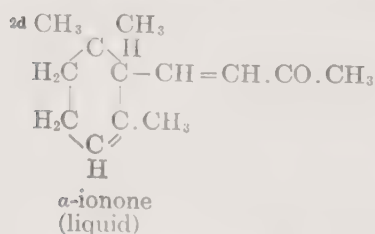
Under perfume sundries any substance is included which enters into the formula for a perfume without directly contributing to its odor. The fixative serves primarily to render the odor more lasting; it is chosen so that it blends well with the oil odor. Three substances have been used for many years past and are still the most important fixatives; these are ambergris, musk, and civet.

Ambergris is a calculus in the stomach of the sperm whale which is formed around a sharp foreign substance such as the beak of the squid, which is excreted and found washed ashore; it may be also cut from the stomach of a whale caught for its oil. Ambergris is dissolved in alcohol and used in tincture form. Its odor is earthy, and its fixative power remarkably great; it is used for the floral perfumes.

Musk is the preputial follicle of the musk deer, found in Tibet and Manchuria; it has not been possible to raise the deer in captivity. The musk pod is situated at the stomach of the deer; each pod yields about an ounce of musk, worth about \$22. The odor of crude musk is disagreeable, but the alcoholic solution after aging several months is not unpleasant. Musk is the fixative for the so-called oriental perfumes (heavy perfumes.)

Civet is obtained from the civet cat, in Abyssinia; crude it is also disagreeable; in the form of aged alcoholic solution, it is used as musk. Frequently both musk and civet are used in one perfume.

Artificial musk is a synthetic product, which has fixative value; the first was musk xylene; the best one at present is musk ambrette, dimethyl-butyl-metacresol-methylether, made from cresol. Among the essential oils, vetivert, orris, and some others sometimes perform the function of fixative.



³ For definition of cracking compare the chapter on petroleum.

iferous resin oils and oleo-resins are important mainly for their odor. Secondary as fixatives. Oleo-resin of olibanum is made from a gum obtained by incisions in the bark of pine growing in the Levant (Asia), the *Boswellia Carteri*. The gum-resin is extracted with alcohol and the non-solubles (gums); the alcohol of the solution is distilled and there is left a viscous mass, the oleo-resin, with the odor of incense. By distilling the gum-resin itself, oil olibanum is obtained. Labdanum is the frankincense of the ancients. Labdanum, found on the leaves and stem of a low plant, yields similarly, oil labdanum. Liquid labdanum also belongs to this class of fixatives.

PERFUMES

Perfumes contain from 2 per cent (weak) to 10 per cent (very strong) of aromatic matter including fixatives; the remainder is alcohol (ethyl). The perfumes imitate single flowers, while fancy or bouquet perfumes do not. As an example for a simple perfume formula, of the floral type, the following is given:

Type of formula for rose perfume—highest type.

	Grams
Oil of rose (the natural floral oil, the otto).....	10
Rose absolute (floral oil, from the concrete).....	10
Geraniol (an isolate)	25
Phenylethyl-alcohol (a synthetic)	20
Oil of geranium (an essential oil)	10
Alpha-ionone (semi-synthetic)	15
Resin of labdanum (resin oil)	5
Tincture of musk	5
Alcohol (90%)	900

This would be a strong perfume of fine quality. Examples of fancy perfumes are Chypre and Ambre, both of the oriental type.

TOILET WATERS

Toilet waters form a class of perfumes by themselves; they are made up of alcohol chiefly; that they are nevertheless called waters is because the French word for water is frequently used for "liquids."⁴ The best-toilet water is Eau de Cologne; the original formula required a distillation, as indicated in the following one, a close approximation:

Bergamot oil	10 cc.
Lemon oil	15 cc.
Lime oil	5 cc.
Orris root	20 grams
Alcohol (90%)	480 cc.
Water	60 cc.

This is permitted to stand 24 hours, and is then distilled; to 480 cc. of distillate there are added

Neroli oil bigarade	3.0 cc.
Rosemary oil	0.5 cc.
Lavender oil French	0.5 cc.
Oil of thyme	0.5 cc.

pour eau de vie, meaning—whiskey or brandy.

The whole is matured one month. The odor is refreshing, not lasting. Eau de Cologne is now frequently made without a distillation. Lavender water is a favorite in England; a simple formula is:

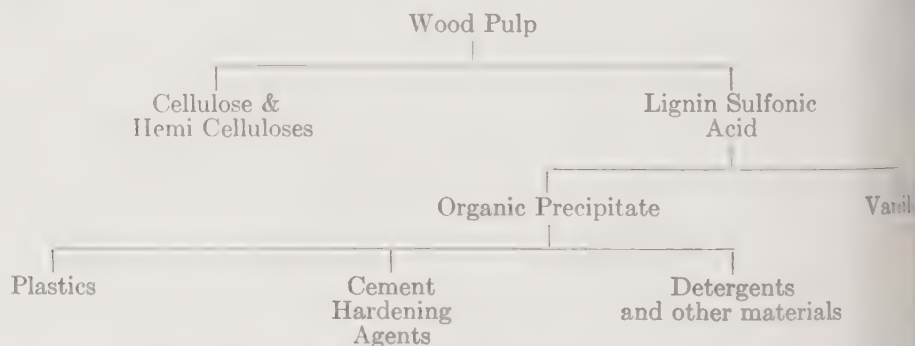
Lavender oil French	20 cc.
Bergamot oil	10 cc.
Sandalwood oil	1 cc.
Civet extract (5%)	5 cc.
Orris resin	4 grams
Alcohol (90%) to make	1000 cc.

Florida water, an American toilet water, contains orange-flower and cinnamic aldehyde, which give it its distinctive note.

FLAVORS

Flavors are used for cooking, for candy, chewing gums, beverages, syrups, dental pastes, and medicines. Oil of lemon, of orange, and of many others have been described; they are obtained by expression, and may be freed from the terpenes. Peppermint is made into *crème de menthe* (Italy). Vanilla extract is perhaps the best-known flavor, and used for numerous purposes. It is made from the vanilla bean, after it has been cured to develop its vanillin content, by extraction with alcohol. The American practice is as follows: 50 pounds of Mexican vanilla beans and 50 pounds of Réunion beans are chipped fine in an automatic cutter, and placed in a "battery" of a cylindrical extractor of steel, fitted with a stirrer. Thirty-five to fifty per cent alcohol is added, in the cold, and stirred for an hour; the extract is run off, and three further extractions made in the same way. The extract is then combined to give the finished material. The amount of 50 per cent alcohol is such that the beans form 10 per cent by weight of the solvent taken. The extract is colored brown by some of the resin which is dissolved.⁵

Vanillin may be made from lignin sulfonic acid, itself obtained from wood pulp; the relationship between several materials obtained from wood pulp is shown on the adjoined chart.⁶



The use of synthetics as flavoring agents is on the increase, as will be seen from the following short list. Methyl anthranilate gives the odor of

⁵ The fresh vanilla bean is green; in size it may be as long as 10 inches; the dried bean is brown. Vanilla beans are shipped tied in bundles of about 30 beans selected of one size. The beans of Réunion, and others, often have a bloom of vanillin on their surface.

⁶ A paper on Lignin-Vanillin delivered by J. M. Wenneis, at the 29th annual meeting of the Flavoring Extract Manufacturers' Association, June 29, 1938; see also U. S. Patent 2,200,187.

ethyl butyrate is basically the odor of rum; saffrole, from brown or oil, is an artificial sassafras, and is used in root beers, candies, herb tonics." Cinnamic aldehyde replaces cinnamon oil, methyl salicylate of wintergreen. Frequently used also is benzaldehyde F.F.C. from chloroform as "oil of bitter almond, artificial."

acetyl $\text{CH}_3 \cdot \text{CO} \cdot \text{CO} \cdot \text{CH}_3$, a yellow, somewhat viscous liquid, and methyl carbinol, a white, thin liquid, are the chief odoriferous flavorer made from sour cream, and are produced by the action of a micro-organism. These two substances are now prepared on a large scale, by the action of the same organisms, in special cultures, and are available for flavorings not prohibited by the pure food laws.

Fig. 75.—U. S. production of synthetic flavors and perfume materials (1940).*

Flavors

	Pounds	
Methyl salicylate	1,641,571	.30
Vanillin	576,708	2.02
Benzyl acetate	246,887	.35
Ethyl butyrate	50,291	.62

Perfume materials

Terpineol	766,705	.20
Geraniol	306,435	0.80
Phenyl ethyl alcohol	193,149	1.91
Ionone	82,568	2.08
Methyl ionone	61,157	2.24
Citronellal	no report	
Citronellol	53,633	1.49
Anisic aldehyde (Aubepine).....	42,218	...
Citral	39,930	1.61
Isoeugenol	25,248	...

* Tariff Commission Report 148.

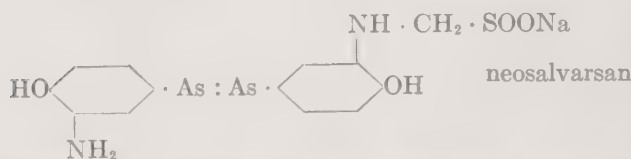
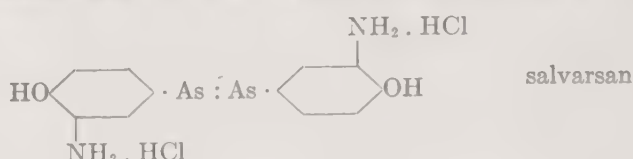
INDUSTRIAL PERFUMERY

Odoriferous substances are being used more and more in the general trades and manufacturing, sometimes to render goods more attractive, often to cover or mask a disagreeable odor inherent in the goods. Examples are: Leather gloves, shoes and handbags, stockings, cotton pads, wall board (to imitate cedar), lacquer, varnishes and leather finishes, cameras, knit goods, sweaters, and tickings, tobacco, rubber, cutting oils and greases, kerosene fly and moth sprays, disinfectants, para-dichlorobenzene, undertakers' specialties, formaldehyde, shoe and floor polishes, floor-sweeping compounds. Perfumes are often used in incense fans, theater sprays and incense. Depending upon the use, the perfume material used will vary from a few cents a pound to \$100 a pound.

PHARMACEUTICALS

A substance used for therapeutic purposes may be classed as a pharmaceutical, so that the list is long. Formerly, pharmaceuticals were extracted from crude drugs of vegetable origin, and to a lesser extent from materials of animal origin (cod-liver oil). Today the natural pharmaceuticals are supplemented by synthetic products, examples of which are given below; at the same time, new successes in materials of vegetable

of animal origin are comparatively recent, for example insulin, from the pancreas of the steer, for diabetic patients. Of the strictly synthetic products, arsphenamine (salvarsan), the specific for syphilis, is of first importance; its modern form is neosalvarsan,⁷ more stable in air. Quinine is from the bark of the cinchona tree, Peru and Bolivia, is an antipyretic, is supplemented by the synthetics acetanilide, used for headache powder (bromo-seltzer), and acetylsalicylic acid (aspirin). The narcotic morphine sulfate, the local anesthetic cocaine hydrochloride, the mydriatic (pupil dilating) atropine sulfate are natural products. Cocaine is now supplemented by synthetic substances, such as procaine hydrochloride (Novocaine), and several other similar products, used in dental surgery. Laxatives are still essentially of vegetable origin, for example cascara sagrada extract and castor oil; of the synthetic laxatives, phenolphthalein

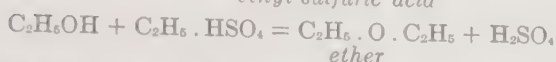
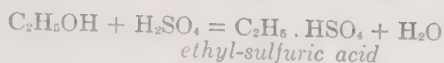


successfully prescribed. Epsom salt is described in Chapter 12. The most important anesthetic liquids, chloroform and ether, which have revolutionized surgery, robbing operations of their terrors, and removing the resistance of the conscious patient, are synthetics of comparatively simple manufacture. As they are both made from ethyl alcohol they might be called semi-synthetics since alcohol is a fermentation product; alcohol may be made from acetylene, when it would be strictly synthetic. The hypnotic paraldehyde is polymerized acetaldehyde, from the distillation of wood; hence it may be called a semi-synthetic. Veronal, a sleeping powder, and saccharin, a sweet non-sugar, are true synthetics. Phenol, formaldehyde, hydrogen peroxide, and iodoform are described in other chapters, radium in Chapter 50.

Ether is made mainly by the dehydration of ethyl alcohol by sulfuric acid; the process is continuous. The sulfuric acid mixed with a certain amount of alcohol is brought to the temperature of 140° C. in a lead-steel boiler by means of steam in a closed lead coil; alcohol is vaporized in a separate vessel and the vapor sent through the acid-alcohol mixture to a still.⁸ There passes out a mixture of ether, alcohol, and water, in vapor form, and these are separated in a column still. The water passes out at the bottom. Alcohol, containing some ether and some water (5 per cent) is removed in vapor form half-way up the column, is condensed and sent over again in the vaporizer. At the top of the rectifier, ether vapors pass out and are condensed in a separate condenser; such ether contains a

⁸ Or an intermediate tower with quartz packing may be used in which the vaporized alcohol with the alcohol, and the mixture overflows in the still proper; U. S. Patent, 1,328,258.

of water and alcohol. Sulfur compounds are removed previously, using the mixed vapors from the still through a dilute caustic solution. The efficiency of the process is high, about 94 per cent. The reactions



Sulfuric acid is regenerated; instead of sulfuric acid, benzene-sulfonic acid has been proposed. A temperature of 128° C. is preferred in a British

process. Ether is lighter than water and forms an upper layer; it boils at 34.5° F., and chloroform boils at 61° C. Ether is widely used as an anesthetic and as a solvent. Of the medicinal grade, 7.97 million pounds were made in 1935 (U. S.), valued at 18 cents a pound.

Chloroform is more rapid in its anesthetic action than ether; it is more acting on the heart action. Both are being supplemented more and more by nitrous oxide mixed with oxygen, even in major operations. The anesthesia is begun with ether, for instance, and continued with nitrous oxide applied at intervals as may be necessary to keep the patient unconscious.

Cocaine hydrochloride is extracted from coca leaves, of the *erythroxylon* and related plants, found in Ceylon, Java, Peru, and Bolivia; the percentage of cocaine base in the leaves varies from 0.7 to 2 per cent. The extraction is chiefly by a mixture of aqueous soda ash and petroleum ether, stirred and constantly agitated in a vessel with stirrer. The alkaloid cocaine base dissolves in the ether, and is precipitated by hydrochloric acid, forming crude hydrochloride; this is filtered, dried, and sent to the refiners in consuming countries.

Acetylsalicylic acid, sold in part under the name of aspirin, is made by dissolving salicylic acid ¹⁰ in glacial acetic acid, in an earthenware-lined vessel, and adding an excess of acetyl chloride. The vessel or still is stirred and the contents are heated until the reaction starts, when the heat may be turned off, for the reaction is exothermic. Hydrogen chloride is carried out through a worm which condenses the acetyl chloride carried out, and reaches a small tower where it is absorbed in water. At the end of the reaction, steam is sent through the jacket and the remaining acetyl chloride is distilled. The crude acetylsalicylic acid is left in the still and purified by solution in alcohol and precipitation by water.

Among the new drugs, sulfanilamide $\text{C}_6\text{H}_8\text{N}_2\text{O}_2\text{S}$, or structurally

 $\cdot \text{SO}_2 \cdot \text{NH}_2$ and sulfapyridine $\text{C}_{11}\text{H}_{11}\text{N}_3\text{O}_2\text{S}$, or structurally

 $\cdot \text{SO}_2 \cdot \text{NH} \cdot \text{C}_5\text{H}_4\text{N}$, both white solids, have rapidly become of

of great medicinal importance.

Choline is made from para-aminobenzoic acid, by forming the di-ethyl-ethyl ester; the resulting base is insoluble in water, but its hydro-

chloride is freely soluble. It is used chiefly in the latter form. A successful introduction of procaine hydrochloride as a local anesthetic, replacing cocaine and partly sold under the name of Novocaine, has led to the preparation of a large number of similar esters, and also of salts with different structures. Like all materials used in pharmacies, a high standard of purity must be reached.¹¹

TABLE 76. *Production of synthetic medicinals in the United States (1940)*

	Pounds	Price
Sulfapyridine	102,196	\$14.89
Sulfanilamide	543,802	1.35
Sulfathiazole (sold)	91,907	14.50
Acetylsalicylic acid (Aspirin)	6,409,824	0.46
Grand total, coal-tar synthetic medicinals..	18,214,431	1.18

* U. S. Tariff Commission Report No. 148.

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¹¹ These standards are listed in the U. S. Pharmacopoeia, 10th edition (1926), obtainable from the U. S. Government Printing Office, Washington, D. C. The newer remedies are listed separately, in "New and Noteworthy Remedies," published yearly by the American Medical Association, 535 No. Dearborn Street, Chicago, Ill.

at the preparation of protective coatings for steel and lumber is an important industrial activity is apparent when it is considered that the interior and exterior of buildings, railway and motor cars, the bottom of ships, and the cables, girders, and arches of bridges are so treated. The chemist-technologist has invaded this field and made important contributions in the form of improvements and discoveries.

Chapter 31

Pigments, Paints, Varnishes, Lacquers, Printing Inks

The pigment industry is usually thought of as associated with paints, but it is really a separate industry, which should be considered by itself, although a considerable tonnage of pigments is mined or manufactured for use in paints, almost as much is consumed in rubber goods, linoleums, oil and artificial leather, plastics, ceramics, and other articles. Among the white pigments, the production of zinc oxide is almost three times that of white lead, which is also surpassed by that of titanium dioxide. When lithopone is added, the total zinc oxide production is about 900 million pounds (1939). Blanc fixe has a smaller production, but barytes are in the same volume class as zinc oxide and lithopone. The production of litharge is about twice that of red lead and other lead oxides, which are 105 million pounds. Carbon black is the leading black pigment. Ultramarine (blue), vermilion (red), lead chromate (yellow), chrome oxide (green) and many others are used for color to a great extent; metallic salts of organic dyes to a decreasing extent. The oxides of iron, both natural and synthetic, are produced in large quantities. For ceramics, metallic oxides are in demand. The uses of pigments in paints, enamels, lacquers, and printing inks is presented in this chapter; other uses of pigments are discussed in appropriate chapters.

WHITE LEAD

White lead is a basic carbonate of lead, that is, a carbonate combined with hydroxide; its formula is $2\text{PbCO}_3 \cdot \text{Pb}(\text{OH})_2$, but the variations are considerable; it is better to remember it merely as a basic carbonate. It is prepared, in one process, by corroding lead in the form of cast buckles by the action of acetic acid and water, in the presence of carbon dioxide emanating from fermenting tan-bark; lead acetate forms first, and this is transformed by carbon dioxide and moisture partly into carbonate, and partly into hydroxide. The buckles are placed in small earthenware crocks 8 inches in diameter and 10 inches high, in which a pint of 28 per cent acetic acid is poured; the buckles lie over the acid, resting on a small shoulder or inner wall of the crock. A layer of these crocks is placed in a thick bed of spent tan-bark, then covered by boards, over which more tan-bark is piled, and another tier of crocks is set in that. This is repeated till five or more tiers are made ready. Some ventilation to the center is provided by a stack-like opening in the middle. The room is then closed. Fer-

mentation proceeds and the temperature rises perhaps to 70°C .; the remain undisturbed for three months. After that time they are unpeeled and the buckles, now white, are lifted out, crushed free from any unroded center, and ground dry or wet. This is the Dutch process. It requires much hand labor, and is slow; but the quality of its product (covering power) is held to justify its continuance. Extremely pure lead is required for this process, otherwise the corrosion does not proceed far enough.

A process which needs no tan-bark and thus avoids an occasional contamination, is the Carter process,¹ in which melted lead is first atomized by superheated steam very much as oil would be in an oil burner, then placed in wooden cylinders lying on their sides and rotated slowly. At intervals dilute acetic acid and carbon dioxide from a coke fire are fed in with some air; after 6 to 7 days, the lead is corroded, and has become white.

In the French process, little time is required; litharge (PbO) is dissolved as a basic lead acetate in acetic acid, and carbon dioxide (fire gas) is pumped into the solution; the basic carbonate precipitates and is filtered off. The lead salts remaining in solution are not lost, for the filtrate is used in making ready the next batch.

For comparison, the stack process (Dutch) requires 3 to 4 months; the Carter process, 1 week; the flue gas precipitation method, 1 or 2 weeks.

In the Rowley process no acetic acid is used; atomized lead suspended in water is exposed to warm air, when the hydroxide forms; carbon dioxide is pumped in for a certain period and white lead of good covering power forms.

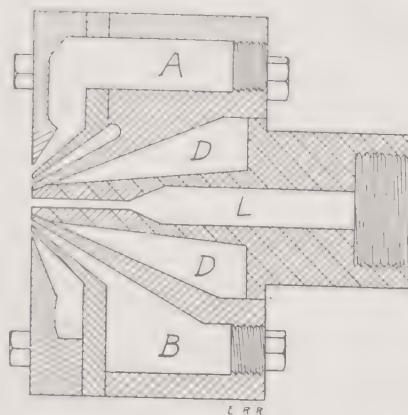
When lead is dry-ground, dust forms, and this is a source of danger because white lead is poisonous; for that reason the grinding is usually done wet. The suspended solid is thickened by settling, giving "pulp"; this need not be dried, if the pigment is intended for paint, so that a paste would be suitable. By mixing the pulp with linseed oil, the oil displaces the water, which rises to form an upper layer, readily run off. The custom is to make a paste containing 92 per cent white lead and 8 per cent raw linseed oil. If the dry pigment is required, dry-grinding is used. The Dutch process at least, is the easiest.

Sublimed White Lead (Sulfate). In any process for white lead, whether metal or the oxide, both requiring a preliminary operation, are employed. If the ore itself could be made into a pigment, that step would be eliminated with consequent cheapening of the product. This has not succeeded with white lead itself, but a pigment close to it has been made. Galena, natural lead sulfide (PbS), is roasted over a carbon fire. The coke is brought to incandescence and the powdered sulfide ore is thrown in at the top, at the same time admitting enough air for oxidation to the sulfate. The reaction is energetic. The product is carried off by the fire gases, which are cooled and filtered (bags); it is a lead sulfate (PbSO_4 75 per cent) and lead oxide (PbO 20 per cent) with some zinc oxide (ZnO 5 per cent), originating from the zinc ore (sphalerite) which occurs in the galenas used. The sulfide and oxide are present in a combined form; the pigment, which has

¹ "The Carter process of white lead manufacture," J. S. Staudt, *Ind. Eng. Chem.*, 1, 758 (1909).

sublimed white lead, is non-poisonous, and is not decolorized by hydrogen sulfide, in these two respects it is superior to white lead.² The process for making "super-sublimed white lead" has been perfected.³ Molten lead is atomized by air under 40 pounds pressure, and natural gas at a pressure of 15 pounds forced in at the outlet from the atomizer (see Fig. 82); a white flame forms, directed in a furnace. Sulfur dioxide is fed

FIGURE 182.—Lead atomizer-burner for super-sublimed white lead; A, gas supply; B, air; L, molten lead passage; D, dead spaces which help keep the lead liquid. (From Dr. Calbeck's article, by permission.)



the flame in the proper volume to produce a basic sulfate of the common $\text{PbO} \cdot 2\text{PbSO}_4$. The dust passes through a cyclone dust box, and goosenecks, and is collected in a bag filter. The brightness of this pigment surpasses that of practically any other white pigment, and its whiteness is superior to that of any lead pigment, comparing favorably with that of the oxide by the French process.

ZINC OXIDE

Zinc oxide is made in several ways. The original one, still in use, is the French or indirect process, in which zinc metal (spelter) is heated in large retorts, the metal vaporized and burned in a combustion chamber at the mouth of the retort. An exhaustor draws the white dust to a chamber first, where the heavier, less desirable particles are deposited, and then to a filter chamber, where the fine dust is collected.

In order to obtain the whitest pigment, a very pure spelter must be used; if it contains lead, for instance, a frequent impurity in zinc, the lead burns large and gives a yellowish tinge, a serious fault. To render the lead less objectionable, a modified indirect method has been developed, in which the burning is done in air mixed with carbon dioxide; the lead is changed to lead carbonate and thus the yellow tinge is avoided. The zinc oxide is unaffected. This modification has been extremely successful and has made possible the use of spelters containing appreciable quantities of lead.

Another modification is to use a retort open at both ends, and to send carbon monoxide at one end and carbon dioxide at the other, which passes over the heated metal and assists in its vaporization. The two burn together as they issue from the

² A. Schaeffer, *Scientific American Supplement*, Nov., 1912, p. 276.

³ L. Calbeck, *Trans. Am. Inst. Chem. Eng.*, 14, II, 13 (1924).

other end of the retort into a combustion chamber; the resulting flame is intense yellow-white. A simple sketch (Fig. 183) shows the disposition of the apparatus. An exhaustor pulls the fumes through a cooling chamber and forces them through bag-filters.

A direct process, that is, one producing the oxide directly from the ore, was developed by Mr. Weatherill about 75 years ago for the New Jersey Zinc Company. In the Weatherill furnace, designed for this purpose, franklinite, an oxide of zinc containing also iron and manganese (Zn 18 per cent), mixed with coal is burned on a grate; the natural oxide is first reduced and then re-formed by the air and carbon dioxide from the fire. Provision is made to admit more air over the fire if unburned zinc vapors should arise. The grate is a casting with tapering holes, not bars. The residue on the hearth is made into spiegeleisen, a manganese-iron containing carbon.

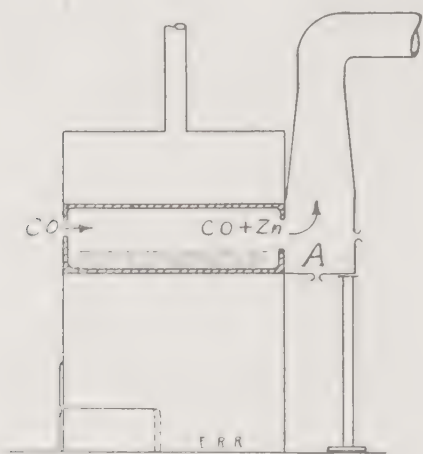


FIGURE 183.—Retort for vaporizing zinc in a stream of carbon monoxide; the two are burned together in the combustion chamber A, to manufacture zinc oxide.

It is feasible to use a low-grade carbonate ore (smithsonite) for the direct production of zinc oxide. In such a plant at Leadville, Colorado, 2 pounds of ore are well mixed with 1100 pounds of coal and wetted to 120 per cent moisture; this batch is shoveled onto the grate of a Weatherill furnace on which a coal fire is burning. Air is forced into the closed combustion pit; the temperature is 1000°C .; the burning requires 6 hours. The gases which pass out with the dust are cooled in a U-shaped 4-foot-diameter flue, 600 feet long. At the end of the trip, the gases are at 140°C .; an exhaustor sends them into cotton filter bags 20 feet high by 2 feet wide which retain the dust, while the gases and water vapor pass out.⁴

Lithopone. Lithopone is formed when a solution of zinc sulfate is mixed with one of barium sulfide; barium sulfate and zinc sulfide are formed; they are both white: $\text{ZnSO}_4 + \text{BaS} = \text{BaSO}_4 + \text{ZnS}$. This precipitate is not suitable for a pigment, however, until it has been dried, heated to a high temperature in a muffle furnace, and plunged when still hot into cold water. Lithopone is 28 per cent zinc sulfide and 72 per cent barium sulfate, with slight variations; it has fair covering power, is brilliant white, and is durable. It is extensively used in interior wall coatings.

⁴ *Met. Chem. Eng.*, 13, 631 (1915).

and fixe is precipitated barium sulfate. The original barium mineral be witherite, a carbonate, or baryte, the sulfate; if the latter, it is and by carbonaceous materials in a furnace, giving the sulfide. The e is dissolved in water, the solution filtered, and treated with, for ble, sulfuric acid, precipitating the sulfate; this is washed and dried. fixe is also a by-product in one of the hydrogen peroxide processes (oter 18).

the capacity and the covering power of blanc fixe are not high; it is eluctly because it is the most permanent white of the white pigments. ed also as a filler in rubber goods, linoleum, etc., and as an indicator ay treatment.

antimony oxide, Sb_2O_3 , is another white pigment now available on a ercial scale; it is used in conjunction with titanium oxide, because it es the chalkiness of the latter pigment.

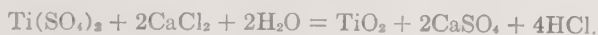
tanium Oxide and Titanox. Until recently a newcomer, but now well ished among the white pigments, is titanium dioxide (TiO_2), which is opaque and hence has a considerable hiding power. In addition to ide itself, a composite pigment is made which has met with success; sists of titanium dioxide precipitated on calcium sulfate or barium e, and is called "Titanox." The use of titanium dioxide in exterior paints expanded when it was found in 1940 that the rutile type of which is more resistant to chalking, could be made by calcining in the ee of antimony oxide, Sb_2O_3 , or other agent; the same product is used ed interior paints without the risk of excessive fading.

he chief ores are ilmenite, FeTiO_3 , the double oxide of iron and m, and rutile, TiO_2 . Ilmenite is obtained from sands in Florida and a deposit in Quebec; it is imported from British India, and up to y from the Malayan states, where it is a by-product in the tin

Rutile is produced in Virginia and Arkansas, and imported from lia. There is a deposit of titanium-bearing magnetite near Tawahus,

ere are two ways to extract the ores in order to form pure titanium e: The ore may be heated in a reverberatory furnace with sodium and coal, the resulting melt lixiviated, and the solution boiled with sulfuric acid; or the concentrated ore may be treated directly with e acid, decanted from undissolved matter, diluted, and the dilute olution boiled; the titanium dioxide precipitates.

prepare the composite pigment with calcium sulfate, the procedure ollows: The concentrate is digested at 100° to 150° C. with 2.5 parts per cent sulfuric acid, and then transferred to a lead-lined vessel. dition of 3 volumes of water, the titanium sulfate dissolves. The equivalent amount of calcium chloride in solution is added, and cal- sulfate precipitates, suspended in the titanium solution. Digesting 5 at 100° C. causes the titanium to separate out gradually, coating the ded sulfate, according to the reaction:



The precipitate is filtered, dried, and calcined; its content of titanium dioxide fluctuates from 20 to 25 per cent, of calcium sulfate from 80 to 75 per cent. The composite pigment with barium sulfate base is made in a similar way. To the solution of titanium sulfate, barium chloride or sulfide in solution is added; barium sulfate precipitates at once, and on that solid, during two hours' subsequent boiling, the titanium oxide is deposited.⁶

Red Lead. Red lead is made from litharge, which may be prepared in several ways. The oldest method, still practiced, is to heat lead metal in a low-arched reverberatory furnace⁷ with the usual bridge wall dividing the fireplace from the hearth. The atmosphere is kept oxidizing by allowing much air to enter; the temperature is just above the melting point of lead oxide, PbO . As the oxide forms, it floats on the surface and is pushed to one side by iron hoes. When enough oxide has collected, it is drawn off by means of the hoes, cooled, ground, and levigated. The color is buff. A continuous furnace has been successful, in which air jets impinge on the surface of the lead so as to sweep the molten oxide to the front end of an oval furnace; fresh lead is added in a stream so regulated that the amount of lead in the furnace remains the same. The molten oxide overflows into a conical receiver; its content when cold is broken up, ground, and floated to remove unoxidized lead particles.

Litharge is also made as a by-product in the manufacture of sodium nitrite. Sodium nitrate is melted in a large iron pot, kept at $340^{\circ}C$. Litharge in thin plates is added. After they have disappeared, the heat is maintained 20 minutes; the brown mass formed is then cooled and extracted with water, and sodium nitrite crystallized from the decanted solution. The residue is litharge; it is washed, and used for red lead or as it is.

Red lead is made by calcining litharge in a muffle furnace into which a muffle of which a current of air is admitted. The temperature must be maintained within narrow limits, near $340^{\circ}C$. The period is usually 48 hours.

Rouge, Fe_2O_3 , is made on the large scale by roasting ferrous sulfate crystals, $FeSO_4 \cdot 7H_2O$, from the pickling vats for steel; water and sulfur oxides are driven off and led through a tall stack to the atmosphere. The familiar red of barns and factory buildings is due to rouge. The shade may be varied considerably by altering the intensity of firing. It is very effective. Its use for polishing glass is based on its freedom from grit.

Ultramarine is a blue; it is a double silicate of aluminum and sodium containing sulfur. The production and use of prussian blue exceeds that of ultramarine. Copper phthalocyanine blues are in good standing.^{8a} Chrome yellow is lead chromate; prussian blue is the iron salt of ferrocyanide; two mixed give a good green, but chrome green is usually made by coprecipitating chrome yellow and prussian blue. Antimony sulfide is yellow; manganese oxide a brown (bister); basic copper acetate is green. Red lead is made by heating litharge as stated in the previous division; white lead is carefully roasted gives a red-orange. Ochres are impure iron oxides, brown to red; they are mainly natural products, but artificial ochres are invading the market.

⁶ U. S. Patent 1,236,655.

⁷ Chapter 4.

⁸ "The lead and zinc pigments," C. D. Holley, New York, John Wiley & Sons, Inc., 1919.

^{8a} *Ind. Eng. Chem.*, 31, 839 (1939); see also Chapter 28.

black, and are finding favor because they are more uniform and no more expensive. Artificial cinnabar, made from mercury and sulfur, is a brilliant red. There are many other inorganic pigments, and they are mixed in every conceivable way. Organic dyes in the form of their insoluble salts with calcium and barium are being used more and more, alone in some cases, and mixed with the usual pigment to brighten the shade in other cases. They are chiefly mono-azo dyes.⁹

Carbon Black. "Carbon black, an extremely finely divided form of carbon (0.025 to 0.05 micron), is made by the impingement of the flame of hydrocarbon gas upon moving metallic surfaces. It should be sharply distinguished from another important black pigment, lamp black, also a carbon pigment, but consisting of the free soot or smoke collected in chambers burning hydrocarbon oils or hydrocarbon gases. The amount of air is controlled, so that complete combustion such as would be insisted on under a blast cannot take place.

Lamp black is the older pigment; it has been made for thousands of years by the Chinese, Egyptians, and other ancient races for the manufacture of ink. Carbon black is a modern pigment.

Carbon black is finer than lampblack, stronger in tinctorial power, and purer in color. In addition to displacing lamp black for inks, paints, and varnishes, carbon black has recently been found to improve enormously the properties of rubber goods; this explains why the rubber industry now takes three-quarters of the carbon black production. The production in the United States follows: 84 per cent of the 1940 production came from the Houston district in Texas.*

	Pounds	Price per pound
Carbon black	525,166,000	2.45 cents
Bone black	29,726,998	4.7
Lamp black	7,842,188	8.7

By suitable changes in the supply of secondary air, the size and shape of tips, distance from, and speed of collecting surfaces, wide variations in color and in other properties of carbon black can be achieved.

Recently new valuable properties of carbon black have been discovered, namely that it improves the insulating properties of rubber insulation and the dielectric properties of insulating (transformer) oils. Carbon black is probably the most finely divided colloid available in unlimited quantities at a very low cost; for this reason there is every likelihood that it will find many new applications in the arts. It is a new material in the world's market, and as such constitutes practically virgin territory for research."¹⁰ "Carbon blacks which have been treated with zinc naphthenate, and "dredged" blacks, from which entrapped air has been removed, can be wetted more quickly and effectively by the vehicle.

Lamp black is made from crude oil or fuel oil, by burning it with an insufficient amount of air and collecting the soot. Thermatonic, or "soft," blacks are also made from natural gas. (Fumonex, p. 33). The white pig-

⁹ Chapter 28.
¹⁰ Bureau of the Census.
 Based on private communication from Dr. W. B. Wiegand.

ments have been discussed in detail; grays are made by adding a small amount of black with some green or brown to the white pigment.

PAINTS

A paint consists of a pigment, a vehicle, and a drier; it is applied to the inside or outside surfaces, and in a day or so hardens to an unbroken film which prevents contact with rain, smoke, direct sunlight, and loss of moisture from the atmosphere; it is a preservative coating. On steel it prevents the rusting and deterioration and destruction called rusting.

The vehicle is usually linseed oil, and this may contain other oils, resins, and driers; such a prepared linseed oil is "boiled oil"; or, raw linseed oil may be used and the driers added when mixing.¹¹ Driers are usually the oxides, resinates, oleates or acetates of cobalt, manganese, lead, and occasionally zinc; they form compounds with the oil and accelerate the oxidation of the oil by the atmosphere. The oil itself does not dry in the usual sense of the word: it hardens by chemical change, or oxidation, accompanied, especially in the case of tung oil, by polymerization.

There are several requirements for a good pigment. It must be opaque enough so that its hiding power may be high; the greater the hiding power, the less paint is required per square foot of surface. It must mix well with the oil. It must be inert to gas impurities in the atmosphere and to the other components of the paint; inertness insures freedom from disintegration. Among other desirable properties it should not darken when exposed to hydrogen sulfide; preferably it should be non-poisonous. Finally, its cost will determine the choice in many cases.

The pigments chiefly used for protection, hence for covering, are white lead, zinc oxide, lithopone, blanc fixe, titanium pigments, and rouge; to these coloring substances are added in small quantities.

Paints are frequently mixed with oil by hand just before using; prepared paints are mixed by machinery; an example will be found under enamels. A balanced paint is one in which the pigments have been chosen to give the paint all desirable properties; for example, among white pigments: white lead, for durability and the protective action of its surface; zinc oxide to harden the film; titanium dioxide, to give lasting brightness.

VARNISHES AND ENAMELS

The materials for varnish-making are certain vegetable oils, resin, a small amount of drier, and a thinner. From the standpoint of the varnish maker, vegetable oils fall into three groups: the drying oils, the semi-drying oils, and the non-drying oils. Linseed oil is a drying oil; when exposed to the air, it sets in about a day and a half. Soybean oil is a semi-drying oil; it requires weeks to dry. Untreated castor oil is a non-drying oil; after months it is still liquid. The drying and semi-drying oils are glycerol esters of unsaturated organic acids; they can take up oxygen and in doing so, harden, which is termed "drying." The non-drying oils are esters of saturated acids and cannot take up oxygen; hence they do not dry.

¹¹ Raw linseed oil and boiled oil are discussed in Chapter 29.

The oils chiefly used in varnish-making are linseed, chinawood (also tung oil), perilla, and soybean (described in Chapter 29). Tung oil heated for 5 minutes to 550° F. (288° C.) cools to a solid gel, whereas oil heated for several hours cools to a viscous liquid merely, indicating how sensitive the former is to heat; both these oils form very durable coatings with phenolic resins.

Perilla oil comes from Manchuria; it dries to a harder film than linseed oil about as fast. Soybean oil has certain unusual properties: it can be heated on heating, and it yellows less fast than any other oil, so that it is used in white enamels. A newcomer is oiticica oil, from Brazil, which dries almost as fast as tung oil.

Hydrogenated castor oil has been developed to take the place of tung oil, but is cut off by the war, since it comes almost entirely from China. All commercial processes involve heating castor oil in the presence of a catalyst (soda ash, silica gel, fuller's earth, sulfuric acid and others) under reduced pressure. Five per cent of the oil is removed as water, leaving conjugated double bonds in the molecule, which hasten drying.^{11a}

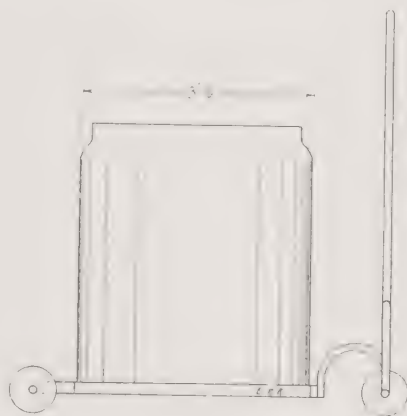


FIGURE 184.—A copper kettle on wheels for varnish-making.

Natural resins are exudations formed on trees long since destroyed by fire; when they lie under a few feet of loose ground they are called fossil resins or copal. The hardest is the Congo copal; there is also a Manila copal, an East Indian copal and a New Zealand copal; the latter is called kauri. There is a variety of copal. To these must be added rosin and ester gum. Natural resins are frequently used in conjunction with synthetic resins, to modify their properties, and to lower their cost (thus rosin is added to synthetic resins).

Synthetic resins have been introduced in varnish formulas in an effort to shorten the drying period; such formulas allow drying within four hours. There are two other points in favor of the inclusion of synthetic resins in varnish formulas: a larger percentage of resins may be incorporated, and synthetic resins absorb ultraviolet light without alteration, protecting the more valuable constituents by their screening effect. At least half the varnishes

C. Weaver, *American Paint Journal*, December 30, 1940; see also "Composition and analysis of hydrogenated castor oil," by George W. Priest and J. D. van Mikusch, *Ind. Eng. Chem.*, 32, 1314 (1940).

are made with oil-soluble synthetic resins. The manufacture of such "oil-soluble resins" is described in Chapter 35 on synthetic resins. In many cases, synthetic resins for molding compounds, a distinct product, are also presented.

To hasten the drying of the varnish, driers are added. Lead, manganese, and cobalt in the form of soaps are used, the amount being very small. For instance, for cobalt, an amount of soap equivalent to 0.1 per cent of oil is sufficient; for lead, 0.5 per cent must be used.

Thinners are introduced so that the oil-resin coating may be applied in thin layers. Turpentine, a petroleum naphtha, or better still, a hydrocarbon naphtha, xylene, or toluene, is used. The petroleum naphtha solvents are particularly well suited to alkyd and phenolic resins.

The relative proportions of oil and resin vary in the several kinds of varnishes. A high-resin varnish would contain to each 10 pounds of resin 1 gallon of oil, $1\frac{1}{2}$ gallons of thinner, 0.4 per cent lead as lead soap. A long-oil varnish would have to each 2 pounds of resin, 1 gallon of oil, 2 gallons of thinner and 0.5 per cent lead as lead soap. A better classification of varnishes is as follows:

"Short"—12-15 gal. oil/100 lbs. resin	for furniture to be rubbed
"Moderately short"—15-25 gal. oil/100 lbs. resin	for many household enameled
"Medium length"—25-35 gal. oil/100 lbs. resin	for spar and floor varnish
"Long oil"—35-50 gal. oil/100 lbs. resin	for durable exterior varnish

In making a "high-gum" varnish, 100 to 200 pounds of resin are placed in a copper kettle on wheels, and this is pushed over the flame of an oil burner set below the floor. The temperature is raised rapidly to 600° (315° C.). Blown linseed oil¹² is now added, and the two together are heated long enough to give a uniform liquid. The driers are next added in powder or liquid form and stirred in; then the kettle is pulled off the fire and cooled in the room. When it is fairly cool the thinner is added, and the varnish is passed through a plate-and-frame press or a centrifuge which retains any suspended material. The clear filtrate is pumped into storage tanks and aged for several months. Numerous laboratory tests have been made on color, clarity, viscosity, specific gravity, drying power on glass, water-proofness and toughness of film.

An *enamel* is a varnish containing a pigment. It is made by incorporating a pigment with linseed oil or varnish or resin solution in a ball mill (for color) or roller mill (for white), followed by further mixing with a varnish in a mixing tank with paddle. The older buhrstone mill is used only for pigments of hardness greater than that of the steel rolls. For whites, white lead, lithopone, Titanox, or blanc fixe is employed.

The roll mill of the older type has three rolls which rotate at different speeds, so that there is a rubbing action which causes unmixed oil droplets to be torn open and brought into contact with the pigment. The rolls are hollow, and water-cooled. The three-roll mill is losing its place in the manufacture of enamels and paints, to the five-roll mill, whose rolls rotate much faster, and whose capacity is three times that of the three-roll mill with the same-sized rolls.

¹² Chapter 29.

Baking japans are varnishes made up with asphaltum instead of resin; baking is done, for metal surfaces, at 400° F. (204° C.) and lasts 3 to 4 hrs. This temperature melts the asphaltum easily, and distributes it evenly; during the baking the oxidation of the oil is rapid, so that on removal of the article the coat is dry. A very beautiful black luster is obtained. By baking at lower temperatures, varnishes containing the usual oil may be used. Such coatings are highly chemical-resistant.

Spirit varnish contains alcohol or similar solvent, and dries by the evaporation of the solvent; it contains shellac,¹²⁰ as a rule, or certain other resins such as mastic, sandarac and dammar. Several new synthetic resins are coming into wide use which might be included under the term "spirit varnish," since they dry by evaporation of the solvent; they are: Cellulose, dissolved in ketones; Pliolite, in hydrocarbons; Tornesit, a chlorinated rubber hydrocarbon, in toluene and xylene.

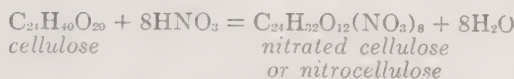
Water varnish contains Chinawood oil and ester gum or reduced phenolic resin, and is waterproof.

LACQUERS

Lacquer is a protective coating which dries by evaporation of volatile solvents and whose essential film-forming constituent is a cellulose nitrate, acetate, or other. The liquid lacquer applied to the surface to be protected contains, for example: (1) nitrocellulose or nitrated cotton, "cotton" for short in the trade; (2) the solvent, usually a mixture of three substances, a ketone, an alcohol, and a hydrocarbon; (3) the plasticizer which remains in the film and keeps it soft; (4) the diluent; (5) a dye or pigment. Table 77 shows the ultimate particle size of the various pigments used.

Lacquer coating dries rapidly, by the evaporation of the solvents; the oil varnish dries slowly, partly by evaporation, partly by oxidation and polymerization.

Nitrocellulose, also called pyroxylin, is made by nitrating cotton linters with mixed acid. The nitration is not allowed to proceed as far as when making nitrocellulose for explosives, for the highly nitrated cellulose (12.5 per cent N and over) is not soluble in the selected solvents; for that reason, "cotton" containing only 11 to 12.4 per cent N is prepared. The linters are purified from oils by boiling with caustic, washed, and if colorless is sought, bleached. The nitration is carried out by placing 32 lbs of cotton in 1500 pounds of mixed acid; the great excess of acid is used to insure negligible change in concentration over the period of nitration due to consumption of nitric acid and production of water.



The reaction given here is an ideal one and is meant to indicate the change that takes place; a single nitrocellulose is really not formed, but a series of

An extensive study of shellac as to its constitution, and uses, is carried on by "The Indian Lac Research Institute," at Namkum, Ranchi, Bihar and Orissa, India, and is described up to the year 1930 in a handsome book published by the Institute. The outlook for continued, in fact, increased consumption of shellac, partly as a result of these studies, is excellent. In conjunction with laboratories at the Research Institute, work on shellac "splitting," and constitution, is carried on at the Polytechnic Institute.

TABLE 77.—Ultimate particle size of various standard pigments.

Materials	Maximum residue on No. 325 screen (opening 44 microns) (Per cent)	Average ultimate particle size (Microns)
Carbon black	1.0	0.1
Fine-particle zinc oxide ("Kadox").....	..	0.12 to 0.18
Zinc oxide (Florence French process "Green Seal")	1.0	0.21 to 0.26
Lithopone	1.0	0.25* to 0.35
Titanium barium pigment	1.5	...†
Zinc sulfide†
High-strength lithopone†
American process zinc oxide	1.0	0.28 to 0.35
Lamp black	1.0	0.4
High-leaded zinc oxide	1.0	0.35 to 0.45
Iron oxide (Spanish)	3.0	0.4 to 0.6
Low-leaded oxide (5% leaded)	1.0	0.50 to 0.65
Sublimed white lead	1.0	0.65 to 0.67
Basic carbonate white lead (Old Dutch Process)	1.0	0.75 to 1.21
Chrome green	2.5
Ultramarine blue	5.0

* According to H. Green, secondary particles (aggregates) of lithopone may be composed of 2 to 50 ultimate particles. When dispersed the individual particles vary in size from colloids to perhaps a half a micron in diameter.
† No definite figures available but approximately the same as lithopone. Table from "Pigments in nitrocellulose lacquer enamels," H. A. Nelson and W. C. Norris, *New Jersey Zinc Co. Research*, September (1927).

them, with various numbers of nitrate groups in the molecules. The nitrogen content is the guide.

After 15 minutes in the acid, the cotton is dropped to a centrifuge belt to remove the adhering acid. It is then beaten in pulping machines (hours), boiled in poaching tubs (12 hours) with several changes of weak alkaline waters. Finally the 25 per cent adsorbed moisture is displaced by denatured alcohol forced in under a pressure of 300 pounds. At this stage the nitrocellulose moist with alcohol resembles cotton waste in appearance. It is made in a few plants, and is bought by the varnish maker who dissolves it and blends it to suit.

Originally the nitrocellulose so made was dissolved in amyl acetate, for example, and articles dipped in the solution. On evaporation of the solvent a film remained. It was soon observed that only 6 ounces of nitrocellulose could be dissolved in one gallon of the solvent; more gave a solution too viscous to flow. In fact, with 6 ounces, the resulting solution was quite thick. Nitrocellulose which gives rise to such solutions is called *high-viscosity nitrocellulose*. It became desirable to modify the nitrocellulose so that a greater amount of it might be placed in solution, and yet have a solution thin enough to be applicable with a spray gun. Such a modified material is *low-viscosity nitrocellulose*, the manufacture of which is described below. It is now possible to place 24 ounces of nitrocellulose with 16 ounces of additional gums in one gallon of solvent, hence 40 ounces in all of a film-forming material, instead of only 6. The important product now is low-viscosity nitrocellulose. The gums which are suitable additions are dammar, shellac, kauri, rosin ester, etc.

High-viscosity "cotton" is still made, for use in bronzing liquid, a

by lacquer formulas, because the film made from low-viscosity cotton is weak.

CONTINUOUS DIGESTER FOR LOW-VISCOSITY NITROCELLULOSE

Nitrocellulose of low viscosity is produced by heating the first product with water under pressure. This was done at first in batch digesters, of small size, then of gradually increasing size as the control of the action was improved. Finally, batch digesters of welded steel, brick-capable of handling a batch of 4000 pounds of nitrocellulose with 1000 pounds of water, were put in successful operation. As the viscosity (that is, the viscosity of the solutions of the treated nitrocellulose) increases with the heating, there is a decrease in the nitrogen content, from 12.25 to 10.05, and at the same time gas forms. In large units of the batch type, venting of the gas formed during the action presents some difficulties. For that reason, and in order to realize the incident economies, a further improvement was sought in the form of a continuous operation.

In the method devised¹³ the suspension of the nitrated cotton (1 part), in the fibrous form, in water (20 parts), is pumped continuously through a tube 1000 feet long, curled back and forth in several tiers, and 12 inches wide, by means of motor-driven centrifugal pumps connected in series. The charge travels constantly and after 25 minutes emerges and falls into a standpipe 200 feet high, from which it overflows to receiving tanks below. Any bubble formed in the heating tube is carried along so that no pockets form. The tube is heated by a steam jacket [to 132° C. (270° F.) for example] for a distance from the entrance to the tube; then insulated for most of the rest of the way, except that near the end it is cooled by a water jacket. An acid-resisting alloy is used. The rate of flow and the temperature are controlled; by keeping them constant, the desired reduction in viscosity is maintained. The excess water is removed by centrifugals, leaving the product moist, or it is displaced by alcohol in a vacuum distilling press, leaving the nitrocellulose alcohol-moist. A test solution is prepared as described below.

Low-viscosity nitrocellulose may also be produced by heating the product with nitration with benzene or ethyl alcohol.¹⁴

The viscosity depends upon the treatment of the nitrocellulose, as has been stated, but it also depends to some extent upon the solvent. The viscosity of the liquid lacquer can be increased by adding non-solvents such as benzene; it can be reduced by adding such "true solvents" as acetone or ethyl acetate.

The falling-ball method is used for testing the viscosities of lacquers. A glass ball $\frac{1}{16}$ inch in diameter and weighing 2.043 grams is made to fall through exactly 10 inches in a glass tube 14 inches high, 1 inch in diameter. The liquid tested at 25° C. (77° F.). The time required for the fall is measured with a stop-watch. The concentration of the "cotton" to be tested, and the nature of the solvent must be specified. The specifications suggested by the Hercules Powder Company have been generally accepted:

"Nitrocellulose of low viscosity," M. G. Milliken, *Ind. Eng. Chem.*, 22, 326 (1930).
U. S. Patents 1,553,494-5.

16 ounces of "cotton" on the dry basis, and as solvent the formula known as No. 366, consisting of ethyl acetate 20, ethyl alcohol 25, toluene 55, all by weight. With the relation given, a solution of a little over 12 per cent nitrocellulose results. In terms of such a solution and of the falling-ball test, a high-viscosity nitrocellulose will require 20 seconds for the fall, a low-viscosity cellulose will be one-half second. Intermediate viscosities are provided.

Plasticizers. By itself, the film of nitrocellulose contracts after the solvents evaporate, so that it wrinkles and buckles away from the surface being coated. This serious defect is successfully counteracted by using the formula a substance which will not volatilize when the film dries, hence will remain in the film, and render it plastic. Such substances are castor oil, camphor, diethylphthalate, dibutylphthalate, diamylphthalate, tricresyl phosphate, tributyl phosphate, butyl stearate, and many others. Castor oil is used, if pigments are to be incorporated in the lacquer. By adding certain substances such as the chlorinated diphenyls, the Aroclors, a decrease in the flammability of the film is secured, in addition to plasticization.

Solvents for Lacquer. The first solvent for nitrocellulose was methyl alcohol and ether; this gave collodion or "new skin." It was improved by the addition of a little castor oil, giving "flexible collodion." For the protective coating, the early solvents were amyl acetate, butyl acetate, and ethyl acetate, the latter two of which are now the most frequently used. The newer solvents are glycol derivatives (Chapter 25), amyl propionate, butyl lactate, cyclohexanol acetate, methylisopropylketone, and many others.

The boiling points of some of the more important solvents are listed below:

Solvent	B. pt.	
	° C.	° F.
Ethyl acetate	77	170
Butyl acetate	125	257
Amyl acetate	137	278.6
Cyclohexanol acetate	170	338
"Cellosolve" (Glycol monoethyl ether)...	134	273.2

A differentiation between the several solvents is well made in two ways: by the vapor pressure at room temperature,¹⁵ and by the rate of evaporation.¹⁶

On drying, too volatile a solvent cools the film considerably, so that atmospheric moisture condenses on it; this is called blushing. The remedy is to use a higher-boiling, hence slower evaporating solvent.

Pyroxylin (the mixed nitrocellulose molecules resulting on moderate nitrating cellulose) placed in a solvent and apparently dissolved, gives merely a colloidal solution, not a true solution. A good solvent is one which takes up a large quantity of nitrocellulose, and still remains fairly fluid; a non-solvent takes up none at all. A diluent is a non-solvent which is miscible with the solvent; it is added in amounts insufficient to cause

¹⁵ Graph on p. 673, *Ind. Eng. Chem.*, 17 (1926).

¹⁶ Graph on p. 500, *Ind. Eng. Chem.*, 20 (1928).

uration of the nitrocellulose. Toluene, benzene, and petroleum naph- are diluents.

Cellulose Acetate Lacquer. Cellulose acetate (Chapter 22) as the main forming material in the lacquer formula has the great advantage that it is not flammable. Two factors, however, have retarded its wider use: one is that, for a given weight of film-forming material, the viscosity of a solution of acetate is not as low as one of nitrocellulose; the other is the higher cost. The plasticizer is generally tricresyl phosphate.

Uses for Lacquer. There are three main outlets for lacquer which involve a tremendous tonnage. First, artificial leather, which is made by coating a cotton fabric with a pyroxylin solution and then embossing to imitate the grain of a leather. Second, the finish for automobile bodies: a nitrocellulose or pyroxylin finish is superior to the standard gum-linseed oil varnish finish in durability, resistance to abrasion, cracking, chalking, and in rapidity and ease of application; it is inferior to varnish in luster. A somewhat duller but more durable pyroxylin finish is now very popular. Third, interior decoration, woodwork, furniture and the like; here lacquer has the advantage over paint that it dries in less time. The application is usually by a spray gun; within a few hours the coating is dry. One coat suffices. Brushing lacquers are also prepared and marketed.

Production figures for pigments, paints, varnishes and lacquers are given in Table 78.

TABLE 78.—Selected items indicating the United States production of pigments, paints, varnishes and lacquers in 1939.*

Pigments		Price per unit
White lead	119,571,570 pounds	5.95 cents
Lead oxide	301,895,235 "	4.8 "
Barium sulfate	313,568,246 "	4.25 "
Carbon black	278,434,200 "	0.85 "
Titanium dioxide	161,708,130 "	10.75 "
Iron oxides, ochres	101,949,630 "	3.21 "
Red lead	196,794,844 "	5.6 "
Lead, other lead oxides	104,881,475 "	6.32 "
White zinc	121,411,553 "	0.69 "
Some yellows and oranges	36,982,940 "	14.7 "
Some blues (prussian blue).....	7,437,542 "	34.7 "
Some greens	10,087,400 "	22.4 "
Mixed and semipaste paints	107,181,630 gallons	146.2 "
Alkyd, synthetic-oleoresinous		
synthetic resins	23,472,584 "	125 "
but 100% natural resins	14,221,132 "	100 "
Cellulose lacquers, clear	13,749,586 "	128 "
but pigmented	12,572,217 "	222 "
Resins, for lacquers	22,386,579 "	63.5 "
Resins, ester gum, natural resin	18,904,915 "	175 "
but synthetic resins	21,340,328 "	201 "
Varnish	7,778,764 "	108 "
Shellac	16,282,716 pounds	19.4 "

* Bureau of the Census.

PRINTING INKS OR NEWS INKS

Printing inks should not be compared to ordinary writing inks; in that they are not inks at all, but rather paints. They must dry as fast as

applied, mainly through penetration of the paper. They are made by mixing carbon black or lamp black with linseed and rosin oils, rosin varnish, and a drier.

Rosin oil is used in part, because it is cheaper than linseed oil. It is made by distilling rosin in simple stills, fired by the staves from the barrels; there pass over water, acetic acid, an impure "pinoline," then rosin oil; the residue is pitch, which is run off hot. The rosin oil is refined by a second distillation. Rosin varnish is made by heating rosin till water, acetic acid, and pinoline have passed over, then running all the residual liquid into a mixer containing warm linseed oil. This linseed oil is previously hardened by the following treatment: It is heated in a kettle over an open burner and when hot enough, flashed, that is, ignited; it is allowed to burn in this way for four hours; then the flame is extinguished by placing a cover over the kettle. Only 5 per cent of the oil is consumed during the burning.

The proper proportions of rosin oil, rosin varnish, and lamp black are first mixed in a preliminary way; then this mixture is fed to a number of small mills consisting of two horizontal steel disks, of which the upper one rotates on its hollow shaft, and drags the lower one, which is larger, with it, but in constantly changing relation. The mixture is fed in from a galvanized pail above, through the hollow shaft. The discharge is at the edge by a scraper.

Colored inks for printing are made similarly, using as pigments metallic compounds of organic dyes as well as inorganic pigments such as Prussian blue and chrome yellow. Some of the organic pigments are Lithol red, lake Bordeaux, Helio fast red.¹⁷

The importance of news ink is indicated in the statement that the *New York Herald-Tribune* alone consumes over 4,000,000 pounds of such ink every year.

OTHER PATENTS

U. S. Patent 2,033,916, organic phosphates, to impregnate wood, and as plasticizer; 1,848,660, process for the manufacture of a red pigment; 1,981,210, manufacture of a green mineral pigment consisting of cobalt chromite and magnesium orthotitanate; 1,846,188-7, production of white pigments from titanium dioxide; 1,833,087, enamel containing barium and strontium compounds; enamel consisting of white lead, zinc oxide, barium fluoride, chinawood oil, linseed oil, turpentine, gum manila copal, etc.; 1,753,616, application of lacquers to metallic surfaces; 1,801,340, nitrocellulose lacquers, and 1,884,255, same, with resins of the coumarin and indene types (*see* Chapter 35); 1,756,100, colored nitrocellulose varnishes; 1,756,101, non-penetrating varnishes and lacquers from reactive resins of the phenol-aldehyde type; 1,817,183, manufacture of lithopone; 1,821,441, paint and enamel with a granulated or powdered base, that can be applied in stippled form; 1,891,079, manufacture of varnish and paint oils, using mixtures of reduced hydrocarbon polymers with varying amounts of drying oils; 1,865,191, a lacquer containing cellulose nitrate, an alicyclic ketone resin and a solvent containing at least 20 per cent propylene glycol diethyl ether; 1,826,667-S, piperidine and anisidine as plasticizer in cellulose acetate combinations, *tri-m*-oxyphenyl phosphate as plasticizer and fireproofing agent in cellulose acetate; 1,870,556 (trichloroacetamide), 1,836,701 (trimethylene glycol diacetate) for similar purposes; 1,836,687, for coating fabrics to form leather substitutes; 1,833,136, for making a sheet material of good flatness of hydrolyzed cellulose acetate.

¹⁷ "The manufacture of organic dyestuffs," André Wahl, translated from the French by F. W. A. London, G. Bell and Sons, 1914, p. 115; also "Printing inks," W. F. Harrison, *J. Chem. Ind.*, 3, 189.

PROBLEMS

One ton of lead in the form of buckles is made into white lead having the composition $2\text{PbCO}_3 \cdot \text{Pb(OH)}_2$. If the yield is 95 per cent, how many pounds of white lead will be obtained?
 With pure materials, what would be the weight of barium sulfate in 1 ton of white lead?
 A rouge which analyzes 92 per cent Fe_2O_3 , the rest water, is made by heating pounds of copperas. How much rouge is obtained?

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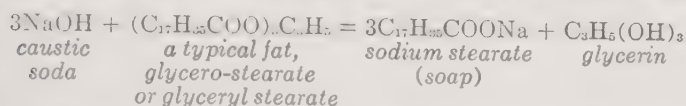
It has been said that the amount of soap consumed in a country is a measure of that country's civilization. There was a time when soap was a luxury; it is now a necessity. The vast amounts of soap now manufactured in every civilized country are possible only because new raw materials have become available through chemical science; the tallows and animal cases of the old days are supplemented by coconut, palm, cottonseed, and other oils.

Chapter 32

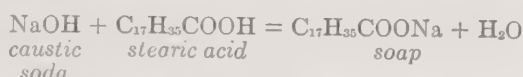
Soap and Glycerin

Soap is the sodium or potassium salt of stearic and other fatty acids: soluble in water, and this solution has cleansing properties which are valued. Other substances cleanse, but soap is the only one which does so without injury to skin or fabric. Other metals also form compounds with fatty acids, for example, calcium, aluminum, and lead; but these compounds are not so soluble, and serve as lubricants,¹ in paints, and for other purposes; they are always designated as "calcium soap," "lead soap," etc.

Soap is made by the action of a warm caustic solution on tallows, fats, and fatty oils, with the simultaneous formation of glycerin which was formerly wasted, or left in the soap, as it still is in certain cases; it now has become a valuable by-product.² The reaction³ is as follows:



Soap may also be made by the action of caustic soda on the fatty acid, when glycerin is produced:



The glyceride used is never a single one, but a mixture of several, so that the soap produced partakes of the properties of each. Sodium stearate dissolves too slowly, and the sodium soap made from coconut oil dissolves too quickly; a mixture of the two has the right solubility. The reaction is generally performed in steel vats, in which a solution of caustic soda is mixed with the fat or oil, and heated; the soap is in solution in the water and may be separated by the addition of salt (NaCl). For high-grade soap, a tank with the upper part stainless steel, is used. The glycerin is dissolved in the water and is drawn off at the bottom. The raw materials are caustic soda or caustic potash (KOH), fats, greases and fatty oils.

RAW MATERIALS

The caustic soda is usually received in drums of 700 pounds of solid soda, and this is made into a strong solution by inverting the opened

Chapter 24. Ordinary soap, that is sodium soap, is also an important lubricant.
¹ 10c a pound.
² Compare the reaction given in Chapter 29.

drum over a steam jet with provision to collect the solution formed. Caustic may also be crushed and dissolved with occasional stirring. Soap plants situated near an alkali factory receive the caustic in the form of a 50 or 25 per cent solution; for long distances this more convenient method would mean a high freight bill. The caustic may also be made at the factory by causticizing soda ash with lime; this is rarely done at present. Caustic potash is usually received as the solid, in drums.

Beef and mutton tallow of all grades are used, from the best No. 1 grade to the cheapest grade recovered from garbage; the grades employed depend upon the quality of the soap to be made. Tallow is not used without admixture with other fats or oils, for it gives a soap which is too hard and too insoluble; it is usually mixed with coconut oil.

TABLE 79.—*Materials consumed in soap-making in the United States (in pounds).*

	1939	1941
Tallow, inedible	785,041,000	1,057,303,000
Grease	120,856,000	310,487,000
Coconut oil	388,912,000	484,124,000
Olive oil foots	19,068,000	10,029,000
Palm kernel oil	3,657,000	1,113,000
Palm oil	102,146,000	129,871,000
Fish oils	114,961,000	69,423,000
Marine animal oils	51,522,000	6,889,000
Olive oil, inedible	1,439,000	555,000
Cottonseed oil	1,061,000	3,010,000
Corn oil	4,441,000	4,948,000
Babassu oil	37,633,000	29,753,000
Soybean oil	11,177,000	24,737,000
Total	1,653,704,000	2,143,857,000

The 1940 total was 1,722,634,000 pounds.

* Bureau of the Census.

Coconut oil is a solid (m. p. 20° to 25° C.); it gives a soap which is fairly hard, but too soluble by itself. It is the basis of marine soaps, and lathers even in salt water. According to the country of origin and to the manner of isolation, coconut oils differ in their content of free fatty acids; the lower the fatty acids, the better the quality of the oil; this applies to all fatty oils. Of the coconut oils, Cochin oil is the highest grade.

Palm oil is usually colored orange to brown, and has 60 per cent of fatty acids, hence does not give much glycerin; it is an important raw material, and is used for toilet soaps. Palm oil may be bleached by warming it and blowing air through it. Palm kernel oil is an oil of light color. Cotton oil is used for transparent soap.

Olive oil of the lower grades, no longer edible, is much favored by the soap maker; for fine toilet soaps olive oil of the edible grade is used, but is denatured by the addition of oil of rosemary, so that its import duty is low. Castile soap is a sodium-olive-oil soap, and also the Savon de Marseille.

In the refining of cottonseed oil a treatment with a solution of caustic is the first step (Chapter 29); the alkaline liquors contain the foots and are used in soap-making. Cottonseed oil itself is also used, usually combined with foots, or after being treated to form the free acids (Twitchell process).

the word "grease" to the buyer of soap stock means an animal fat, rather than tallow, obtained by rendering diseased animals, or from house-municipal garbage, from bones,⁴ and tankage. Sales in 1939 of "grease making soap stock" were 154,870,960 pounds, at 4.7 cents a pound; while "w, inedible," also a soap stock, was 781,962,229 pounds, at 5.03 cents a pound. Rosin serves for laundry soap, and is discussed under that heading.

Free Fatty Acids. Instead of the glycerides, the free fatty acids may be used; these are produced in a preliminary operation, the best known of which is the Twitchell process.⁵ (See Fig. 185.) In this process, any qual-

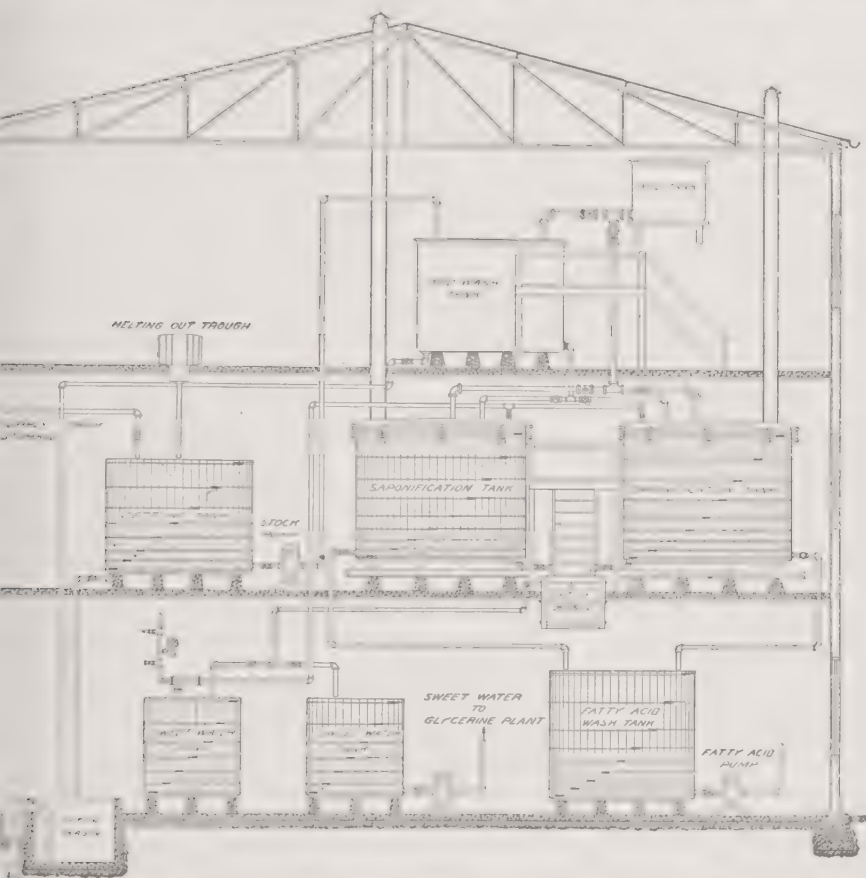


FIG. 185.—Twitchell process fat-splitting plant, with settling tank, two saponification tanks, sweet water tanks, and fatty acid wash tank. (Courtesy of Wurster and Sanger, Inc., Chicago.)

oil or grease is changed into slightly colored free fatty acids. Glycerine is recovered from the acid liquor, and "candle tar," a second by-product, is the residue of the distillation of the crude fatty acids. The process consists of treating the fats or grease with 30 per cent sulfuric acid in the presence

Chapter 36.
T. Joslin, *Ind. Eng. Chem.*, 1, 654 (1909); also "Thomssen's soap-making manual," New York, Nostrand Co., 1922.

of a small amount (0.5 or 1.0 per cent) of the catalyst; the boiling is done in open, lead-lined wooden tanks. The reagent or catalyst is made by sulfonating a mixture of oleic or other fatty acid and naphthalene. (U. S. Patent 601,603 [1897].) The melted fatty acids produced, insoluble in water, are freed from acid by water addition; the sulfuric acid waters containing the glycerin; by adding lime, the sulfuric acid is precipitated as calcium sulfate, filter-pressed, and the glycerin recovered from the filtrate by concentration. The fatty acids are agitated with water to remove any residual sulfuric acid, and used as such, or they may be distilled under very low pressure (10 to 20 mm. Hg); the still is heated by open fire (obsolete), superheated water circulated in coils cast into the bottom of the still (Franklin), or, by means of Dowtherm in free or cast-in coils. The latest is continuous distillation with a column still, as shown in Figure 186. The injection of steam into the acid during the distillation is common to all procedures, and all are vacuum distillations. The distillate should be white

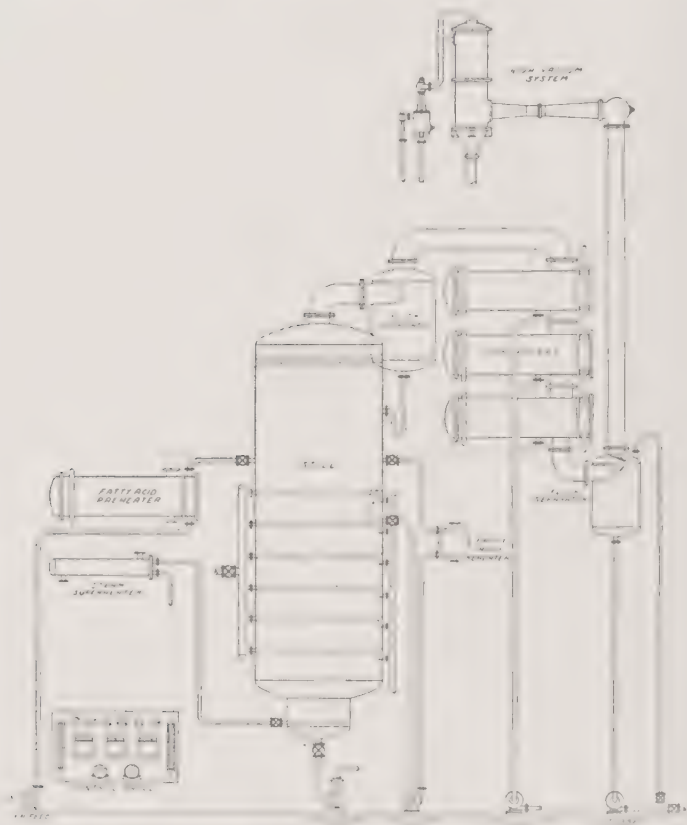


FIGURE 186.—Continuous fatty acid distillation plant with column.
(Courtesy of Wurster and Sanger, Inc., Chicago, Illinois.)

but often is yellow or brown; the Twitchell process produces a fatty acid which tends to be dark. The residue in the still, the candle tar (or steam pitch), is used for prepared roofings. The reagent is not recovered. Steam acid produced by this process is an excellent material for making candles; it is a white solid when pure, melting at 69°C . (156°F .). Commercial

acid melts at 65° C. (149° F.) or lower. The fatty acids produced be liquids or soft solids, as well as hard solids, and serve many uses.

Several advantages are claimed for the Twitchell and similar processes. Concentration of the glycerin is higher in the filtrate from calcium sulphate than in the glycerin water in the boiled process, and it is free of salt. Fatty acids may be made into soap by means of soda ash; the more caustic is not necessary. There is a decrease in the odor of strong-smelling stocks.

MANUFACTURE OF SOAP

Ordinary toilet soaps and laundry soaps are made by the "boiled process," which is adapted to batches ranging from 1000 to 800,000 pounds; and for special process, the "cold process," is used for special soaps.

In the boiled process, a batch of 300,000 pounds of soap, for example, may be made in a steel kettle 28 feet in diameter and 33 feet deep, with a conical bottom. A solution of caustic soda testing 18° to 20° Bé. (14.4 per cent NaOH) is run into the kettle, and the melted fats, oils, or oils pumped in next. The amount of caustic is so adjusted there is just sufficient to combine with all the fatty acids liberated. Steam is supplied by direct steam entering through a perforated coil laid on the bottom of the kettle. There is no stirrer, but agitation is provided by a steam jet entering at the base of a central pipe (see Fig. 187). The kettle is kept boiling until saponification is complete, which requires about 8 hours; salt (NaCl) is now shoveled in, allowed to dissolve, and the boiling continued until the soap has separated, forming the upper layer. The lower layer contains glycerin and salt, and is drawn off at the bottom of the kettle; its concentration is described under glycerin. The whole operation just described is termed the *saponification change*, and requires about 8 hours. The salt used is chiefly rock salt; most of it is recovered and used over again. On the second day, water is run in and boiled with the soap; any glycerin still in the soap is dissolved, and the solution, a lower layer again, is run off from the bottom; it is combined with the first glycerin water.

On the third day, a 10° Bé. fresh lye (6.5 per cent NaOH) is run into the kettle and boiled with the soap. Any glyceride which escaped the first change is saponified; any uncombined free acid is neutralized. The soap, which is not soluble in the alkaline liquor, acquires a grainy structure. This is termed the *strengthening change*. After settling, the lye is run off and used for the next batch.

On the fourth day, the soap is boiled with water, which is chiefly incorporated in the soap. By this treatment the melted soap acquires a smooth, glossy appearance. On settling, three layers are formed: the upper layer, the melted soap; the middle layer, the *nigre*, which consists of a mechanical mixture of soap in a soap solution; and a very small lower layer containing alkali. The melted soap is pumped away by means of a swing pipe without removing the *nigre*; the latter may remain in the tank and be added into the next batch; the small lower layer is wasted. This operation

is the *finishing change*, and lasts several days because the settling is very thorough. For the whole cycle of operations, about one week is customary.

The melted soap is pumped to driers, crutchers, or storing frames. It contains 30 to 35 per cent water. One pound of fat or grease makes about 1.4 pounds of kettle soap; the factor varies with different raw materials.

Laundry Soap. The procedure for laundry soap by the boiled process is the same as has just been described, but the raw materials are, for example, 4 parts tallow and greases and 2 to 3 parts rosin. The latter is added after the greases have been saponified, in the form of sodium resinate; it is made in a separate kettle, by the action of soda ash (which costs less than caustic) on the rosin. A saponification does not take place with rosin, which consists chiefly of abietic acid, and not glycerides; the formation of the sodium resinate is rather a neutralization. Rosin is cheaper than grease, and gives a rather soluble soap.

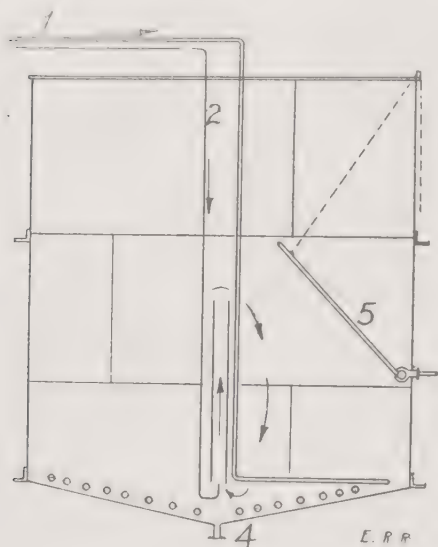


FIGURE 187.—Kettle for soap by the boiled process: 1, steam inlet for the perforated steam coil; 2, steam for agitation; 4, run-off for lye liquors and glycerin liquors; the soap is pumped out through the swing pipe 5.

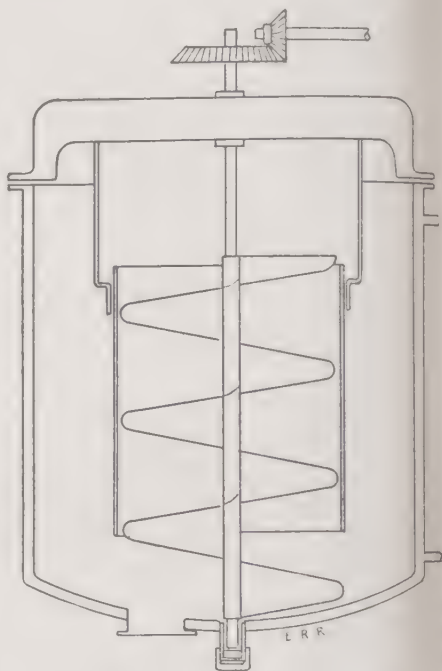


FIGURE 188.—The soap crutcher.

The kettle soap for laundry is pumped from the kettle to a crutcher, which is a smaller tank (Fig. 188) fitted with a special agitator and with a steam jacket, and one of the following materials is added: silicate of soda, 41° Bé. (with 40 per cent solids), up to 30 per cent; soda ash, 2 to 5 per cent, either alone or with borax, 1 per cent; or trisodium phosphate, up to 5 per cent. The mixture is crutched until homogeneous; it is then run off at the bottom of the crutcher into a "frame," a box 4 feet high, 5 feet long, and 15 inches wide, with removable sides, two of metal and two of wood; it

⁷ Normally \$10 to \$14 for a unit of 280 pounds; while tallow and greases average 5 or 6c a pound.

a small truck. The content of such a frame, of which there are four, is 1000 to 1200 pounds of soap. A crutcher $4\frac{1}{2}$ feet high and $3\frac{1}{2}$ feet in diameter has a capacity slightly greater than that of one frame. The content of the frame hardens in 3 days to a solid block, and the sides of the box may then be removed. The block is dried somewhat, then cut into slabs, and these into bars and pieces. The water content of the finished soap is about 30 per cent.

Milled Toilet Soap. For a milled toilet soap, the kettle soap is shredded, dried, mixed with essential oils, milled in stone mills, plodded, thatched into bars, and these cut into cakes. A milled toilet soap contains 15 per cent water.

The kettle soap is pumped directly into the operating tank of a French American soap drier (Fig. 189) and from there fed gradually to a series

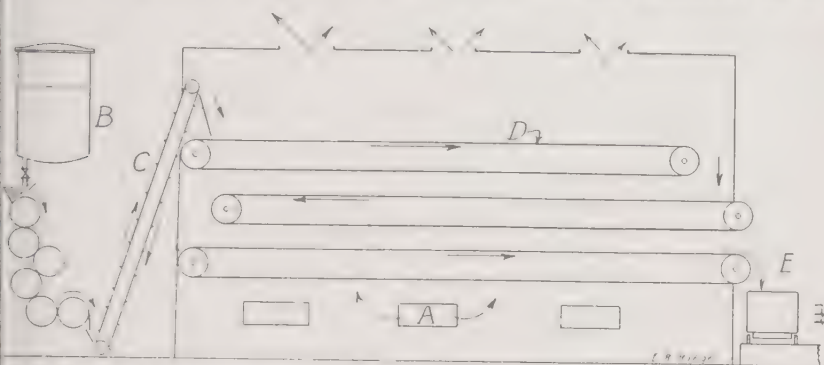


FIGURE 189.—An American soap shredder and drier. The melted soap from the insulated tank *B* is fed to the chilled rolls, reaching the knife where the ribbons are formed; they are elevated by *C* to the wire screen *D*, passing to the other two and discharging at *E*; the warm air enters at *A*, and leaves at the top.

of rollers, chilled by ice-cold water. The film hardens, and passes six times, each rotating a little faster than the preceding one. The last roller is provided with a knife with saw-tooth edge, which tears the soap into ribbons $\frac{1}{8}$ inch wide. These are elevated by a broad endless belt with wooden rollers to the uppermost of three horizontal endless wire belts. The soap drops from the first wire belt to the second, then to the third, which carries them, warm, to a receiving box on wheels. The wire belts are housed in a wooden closet, and warm air is forced through them, reducing the moisture of the ribbons from 30 to 15 per cent. They are next fed to a granulating mill, consisting of 8 granite rollers. The ribbons are sprayed with the essential oil chosen, as they enter the mixer; in the passage between the rollers, which again move at increasing speeds, they are pressed together and mixed thoroughly. On leaving the last roll, a serrated knife cuts the soap into formed sheet into ribbons again. These are still warm, and have the moisture content so that when fed to the next machine, the plodder, they palesece perfectly on being forced by a spiral screw through a die; the soap is conveniently stored in the form of solid blocks made in the special box described for ordinary soap as a frame; when needed, the blocks are cut in slabs, and these remelted in a kettle.

screw and die are steam-heated. A bar is obtained which can be cut into cakes by the movement of a frame with taut steel wires. Each cake is then pressed in a die to receive the trade mark and its final shape.

Cold Process Soap. In order to make soap by the cold process, a vertical crutcher such as described under laundry soap and shown in Figure 119 may be used (capacity 1200 pounds), or a horizontal one of greater capacity. The fat is run in and heated to 130°F. (54°C.) by the steam in the jacket; then the lye is added and the mass agitated. The reaction is exothermic, so that the heat may be turned off at this point. After crutching for about an hour, the mixture stands for $3\frac{1}{2}$ hours; then it is agitated again, and again rested. The glycerin liberated remains in the soap, which is run off at the base of the crutcher into frames and milled as described under milled toilet soap; or the perfume may be added in the crutcher, mixed with the mass there, at the end of the operation.

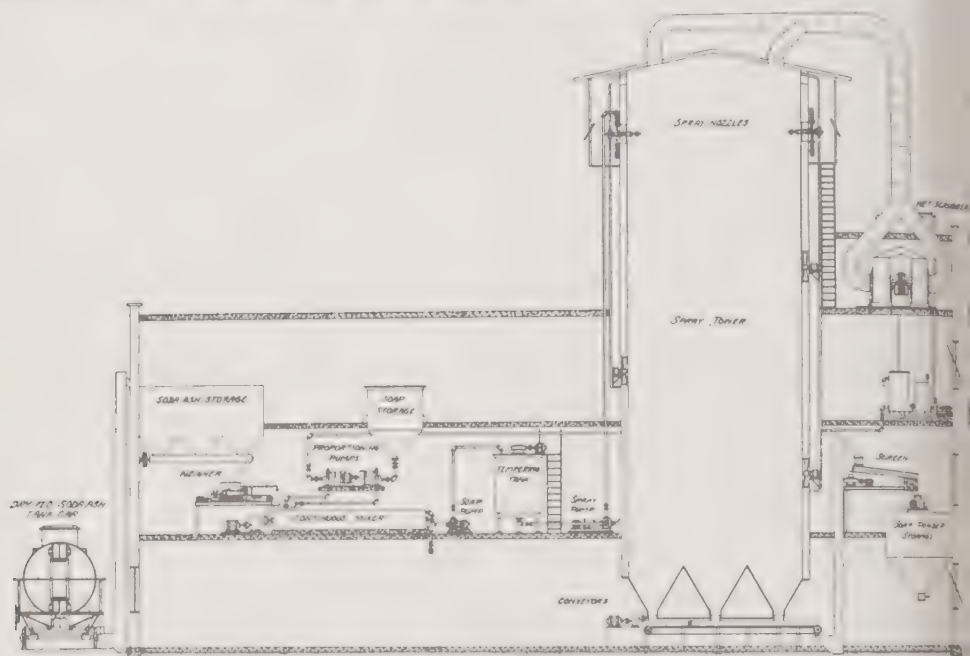


FIGURE 190.—Wurster and Sanger continuous spray-process soap powder plant. (By permission.)

Sodium and potassium soaps mixed are always made by the cold process. Potassium soaps are soft soaps; the potassium soap cannot be salted out by NaCl , for the sodium soap forms; neither can it be salted out by potassium chloride, KCl . The process is used for shaving soaps, toilet soaps, and special soaps; certain laundry soaps are also made by this method. Shaving soap is a potassium-sodium soap containing free stearic acid in order to give the lather a lasting property.

Miscellaneous Soaps. Transparent soap is made in a variety of ways. One method requires the best coconut oil, castor oil, and tallow, which are treated with caustic soda lye by the cold process; the glycerin remains, and cane sugar and alcohol are added.

up powder" is a hydrated mixture of soap 20 per cent, soda ash 10 per cent, and the remainder water. Powdered soap is very dry soap which has been reduced to a fine powder; it is used in dispensers in wash-basins.

Liquid soap is usually a potash soap dissolved in water, containing from 10 to 30 per cent, the solutions of 30 per cent and higher contain alcohol. The manufacture of soap powder may be illustrated by means of the spray system, shown in Figure 190.

The soap powder, containing, for example, 20 per cent soap and 40 per cent sodium carbonate, is sprayed into the tower through a special nozzle. As the small drops travel downward, they cool, partly by losing heat to the air current which sweeps upward, partly by evaporation of water. The sodium carbonate crystallizes to $\text{Na}_2\text{CO}_3 \cdot 10\text{H}_2\text{O}$, sal soda, leaving the greater part of the water; only a small amount need be evaporated to produce a dry powder.⁹

Textile soap is another specialty soap; it is made from olive oil, and is packed into barrels so that the buyer receives a cake the size of the barrel, which can be cut into slabs and bars to suit his requirements. Textile soaps for wool, silk, or cotton differ and formulas suitable for each are recommended.¹⁰

TABLE 80.—Selected items in the soap industry for 1939.*

Bar soap	Pounds	Value per pound
Toilet soap	405,083,669	16 cents
Laundry soap, white	660,766,458	4.52
yellow	580,215,263	4.79
Granulated, powdered and sprayed soap	894,727,289	8.45
Soap chips and flakes, packages	284,143,533	8.28
bulk	135,071,434	7.1
Washing powders, packages	133,638,514	4.12
bulk	114,703,458	2.9
Scouring powders, packages	167,441,482	4.15
bulk	18,708,354	4.26
Textile soap	63,671,392	7.89

Source: Bureau of the Census.

OTHER PROCESSES FOR LIBERATING GLYCERIN FROM FATS

The lime soap process, used in Europe, has been tried by at least two firms in the United States; by one of these, its use has been discontinued. In this process, the fats are saponified by lime instead of caustic; the insoluble soap forms and separates without requiring addition of salt. The glycerin liquor is therefore free from salt and its concentration much increased. The lime soap is changed to sodium soap by treatment with soda ash.

Another process, used chiefly in Europe, is the autoclave process; like the lime process, it is designed to produce a purer glycerin than is yielded by the boiled soap process. The fats or oils are heated with water, and a small amount of lime, or lime and magnesia, for several hours in a closed vessel generally made of copper; the fats are hydrolyzed, resulting in the formation of the free acids, glycerin, and a moderate amount of calcium soap.

U. S. Patents 1,732,454 and 1,740,759.

See "The soap-maker's manual," New York, D. Van Nostrand Co., 1922.

cium and magnesium soaps. The soaps and the free acids separate as solids from which the glycerin water may be decanted or separated by pressing. The hydrolysis may be performed with water alone. The glycerol obtained by this process is purer and of a better color than that obtained in the Twitchell process.

The really modern process is a continuous one, as for example, Eisenlohr, in which a mixture of fat with at least the same volume of water is pumped through Inconel coils heated with Dowtherm to a temperature of about 650° F. (343° C.) under a pressure of 3,500 psi. Hydrolysis takes place without any reagent.¹¹ A number of details of this process will be obtained from Figure 192; the rate of flow of the fat and water mixture through the reactors is quite rapid, so that the material is in the coils only a few minutes, and a state of turbulence is maintained.

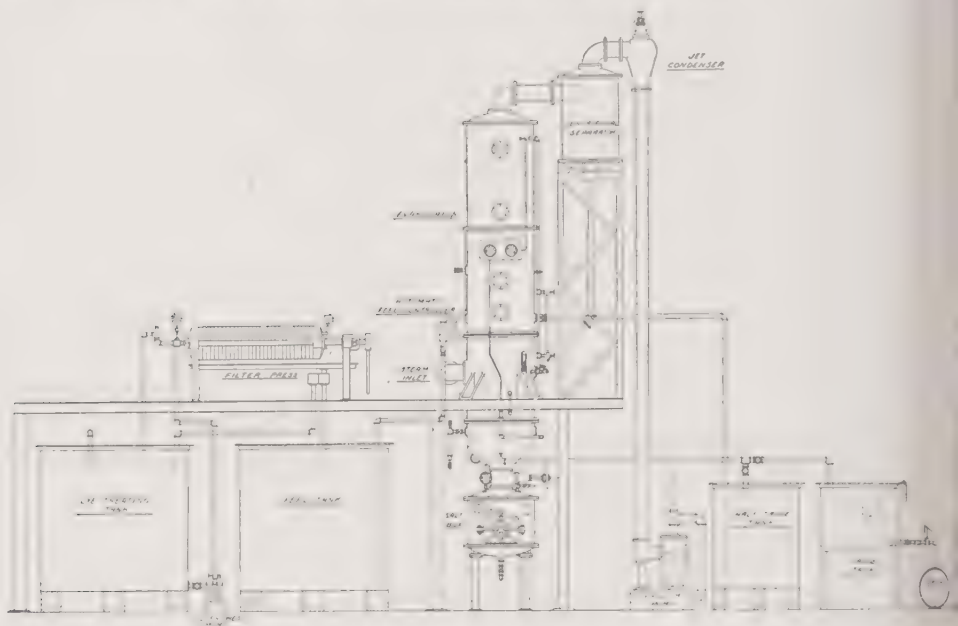


FIGURE 191.—Spent soap-lye glycerin treating and evaporating plant. Steam chest in evaporator not shown. Note salt box under evaporator. (Courtesy of Wurster and Sanger, Inc., Chicago, Illinois.)

GLYCERIN

Crude Glycerin. The spent lye drawn from the kettle in the boiled press contains the glycerin (5 per cent), the salt (10 per cent), some aluminous substances, free alkali, and soap in solution. The alkali content is normally 0.4 per cent or less; for purification, aluminum sulfate is added. There are formed aluminum hydroxide and aluminum soaps, both insoluble. This precipitate settles well in the slightly acid solution; it is filter-pressed and the filtrate made slightly alkaline before concentration. (See Fig. 191.) The concentration is performed in a closed, upright cylindrical steel vessel with conical bottom, and fitted with a steam chest. The steam in the chest is low-pressure, 5 to 25 pounds; this is sufficient because the pressure on

¹¹ U. S. Patent 2,154,835.

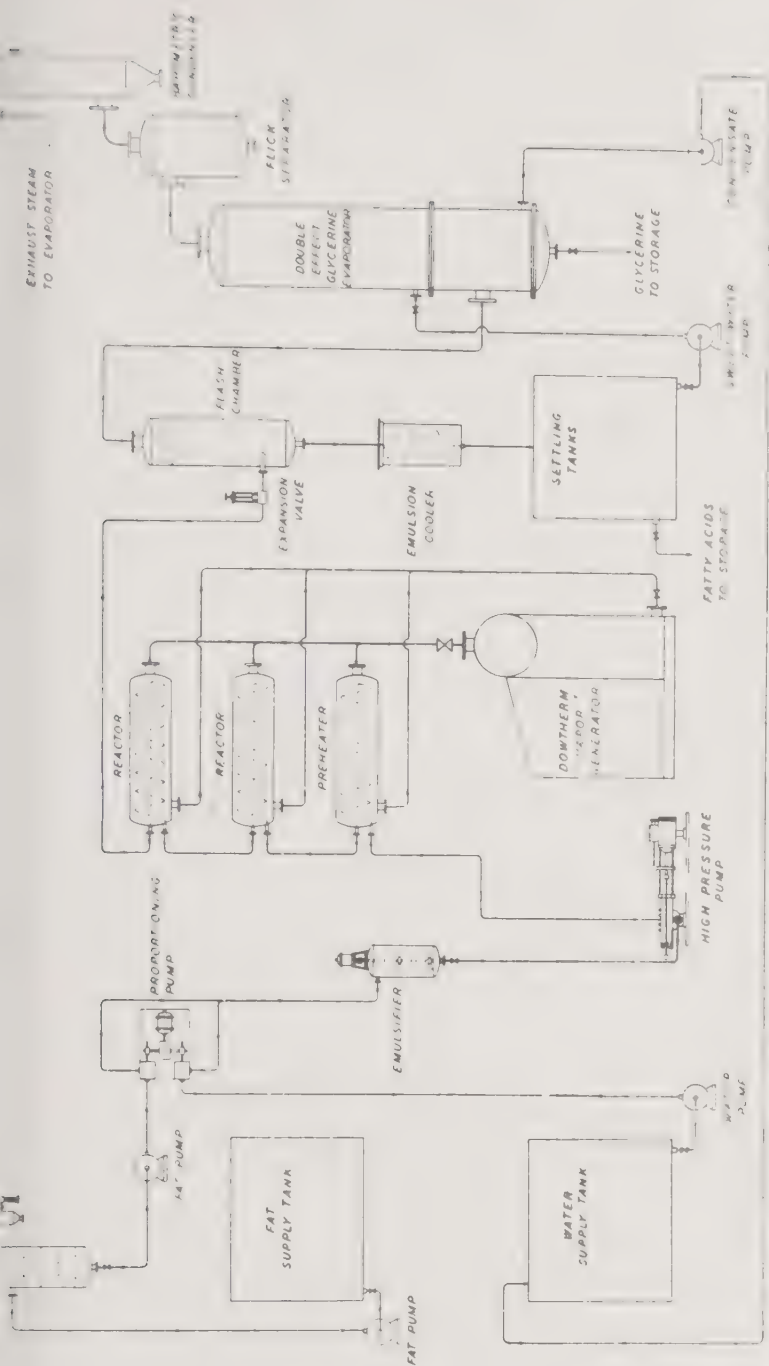


FIG. 14. 192. Diagrammatic drawing of the Eisenlohr process for hydrolyzing oils and fats. A mixture of water and oil is pumped into the reactor, consisting of pressure coil and shell; the heat is applied by means of Dowtherm. (Courtesy of Wunster and Sanger, Inc., Chicago, Ill.)

liquid is reduced by a vacuum-producing device, usually a steam jet, to well below atmospheric. Water vapor passes out, and when the specific gravity of the liquid has reached 29° B \acute{e} , the salt can no longer be in solution, and separates, dropping into the cone. The whole content of the evaporator is dropped into the salt box, a box with a false bottom covered with a filter screen; in this salt box, the salt settles on the screen, and clear liquor is sucked from below the screen into the still; glycerin from the soap kettle is run onto the salt, this suspension settled again, the liquor also sucked into the still. The salt, now fairly free from glycerin, is blown with steam, and then discharged by hand labor; it still retains 10 per cent of glycerin or so, but this is not lost, for the salt is used over and over again in the kettle room.

The liquid drawn back into the still from the salt box is much lower in specific gravity, for it has lost the salt; its glycerin content is about 40 per cent. The evaporation is continued until 80 per cent is reached, and the red liquid then obtained is the "soap lye crude glycerin" of commerce. A test for this stage consists of heating a small sample in an open dish; a boiling point of 158° to 160° C. must be reached.

When the salt drum is used, the salt is allowed to collect in the bottom as it forms, until the drum is filled with a salt sludge consisting of salt and in the thickened glycerin. The sludge is then blown into a hopper from which it drops to centrifugals; the glycerin is returned to the evaporator, the salt washed with a little water and discharged. In this operation the salt drum functions as a blow case. A rotary drum suction filter can replace the centrifugal.

There is a second kind of crude glycerin, the "saponification crude" produced by concentrating the glycerin waters from the catalytic, autoclave, or continuous processes for fat-splitting. Soap lye crude contains 80 per cent glycerin; saponification crude 88 per cent.

Crude glycerin is the raw material of the glycerin distillers, a separate enterprise. Many of the larger soapmakers, however, distill the glycerin in their own plants.

Distillation of Glycerin. The crude glycerin with a red color is changed into a purer straw-colored glycerin by distilling it under reduced pressure in a current of steam. The still is heated by a steam coil in which pound superheated steam circulates; the pressure is made as low as possible, about 1 inch of mercury,¹² or 25 mm. The water contained in the crude glycerin comes over first; after this is over, the steam jet adding wet steam to enter the liquid is turned on and the glycerin comes over with the steam. The vapors pass through five air-cooled receivers in which the glycerin, with a little water, condenses, but which cannot hold the water of the water vapors; these pass on to a multi-tubed cold-water condenser with considerable surface, where it is condensed rapidly. The condensed water, containing some glycerin, is termed sweet water; its amount is not considerable, for about 3 pounds of steam are sent through for each pound

¹² This means absolute pressure; the usual statement is 28 inches vacuum; if the normal atmospheric pressure at that locality is 29 inches, it is the same as 1 inch pressure absolute. The barometric pressure at sea level is 29.92 inches Hg.

rin. The sweet water is evaporated to the strength of crude glycerin and is concentrated in the same way.

Glycerin gathered from the air-cooled receivers has a concentration of 99.8 per cent. By far the greater quantity is made into dynamite glycerin, concentrating it again at reduced pressure, pulling away the water vapors. The content of glycerin is 99.8 to 99.9 per cent, and the specific gravity at 15° C. Dynamite glycerin is straw-colored.

There are left in the still a residue, the foots, which contain the sodium formed by the aluminum sulfate treatment, glycerin, and organic residues. The foots are treated to recover the glycerin content.

Distilled glycerin is made into the U.S.P.¹³ grade by treating it with lukewarm water, with bone char, filtering, and redistilling the filtrate in a still used for nothing else. The distillate is treated with bone char a second time, filtered, and is then as white as distilled water. It has a content of about 98 per cent, and a specific gravity of 1.258 at 15° C.

The yield of glycerin as dynamite glycerin or U.S.P. glycerin is about 98 per cent of the glycerin contained in the solution from the soap kettle.

The process for the manufacture of glycerin by the fermentation of sugar has been put into large-scale practice. A yeast is used, and fermentation is made to proceed in an alkaline medium by the addition of sodium sulfite, sodium phosphate, sodium carbonate, or any one of several other salts. Sugars which are suitable are grape sugar, glucose, fructose, inverted saccharose, treated starch. One kilo of sugar to which have been added 500 grams of sodium sulfite anhydrous, and 250 grams of magnesium sulfate, in 8 liters of water, with 100 grams of yeast, yielded in the first trial 13 per cent ethyl alcohol and 33 per cent glycerin.¹⁴ An improved yeast which will bring about the fermentation of sugar to glycerin in the normal time has been described.¹⁵

Glycerol is produced synthetically by the hydrogenolysis of carbohydrates such as cornstarch; the crude product may be purified by crystallization so that it may meet the U.S.P. specifications.¹⁶

Glycerin is made by a number of other synthetic chemical methods. One of these starts from propylene, a refinery by-product; by "hot chlorination" followed by treatment with hypochlorous acid and a hydrolysis, the glycerol molecule is formed.¹⁷

Glycerin is used for dynamite manufacture, in paper making, in the manufacture of rayon, Cellophane, and in certain inks. It finds use in automobile brakes for automobiles, and in certain shock absorbers. The highest grade is used in pharmacy. Glycerin is valuable also as a solvent; in an anti-freezing mixture in automobile radiators it has found use in the past, but synthetic ethylene glycol has largely displaced it.

In 1939, there were produced in the United States 29,461,738 pounds of glycerin (80%) valued at 8 cents a pound; 64,293,972 pounds of

United States Pharmacopœia, see Chapter 30.

Patent 1,511,754.

Patent 1,551,997.

"Production of glycerol by crystallization," by H. B. Hass and J. A. Patterson, *Ind. Eng. Chem.*, 41(1).

"Synthetic glycerol from petroleum," by E. C. Williams and associates, *Chem. Met. Eng.*, 47,

dynamite glycerin, valued at 10.25 cents a pound; 90,484,348 pounds of chemically pure glycerin, valued at 10.5 cents a pound.

OTHER PATENTS

1,852,820, manufacture of a stabilized soap containing phenylbenzoate; 1,852,821, on manufacture of resinous soaps; 1,887,743, transparent or opaque toilet or medicated soaps; 1,874,388, rapid, continuous process and apparatus for making intended to replace the cold process; 1,885,166, distillation of glycerin by a superheated steam; 1,837,010, production of pure glycerin.

PROBLEMS

1. A soap powder is to be made from a soap solution containing 20 per cent and 40 per cent sodium carbonate. Let all of the sodium carbonate be transferred into crystals of the decahydrate, and let the soap retain 5 per cent moisture. Much water will have to be lost by evaporation in order to reach apparent dryness of the powder?

2. Let saponification reaction take place as stated in the introduction to chapter, in the first reaction, with a fat. If 1200 pounds of NaOH (100 per cent) consumed, how many pounds of glycerin are produced? If the caustic is in the form of 18° B_é solution with 12.6 per cent NaOH, and the kettle has three times capacity of the caustic solution, what would be the necessary size in cubic feet? What dimensions which will reflect the shape of kettle shown in the illustration in the chapter?

READING REFERENCES

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er since the birth of modern chemistry, which is usually dated from the death of Antoine Louis Lavoisier, late in the 18th century, the men practicing the new science have controlled the manufacture of explosives; Lavoisier himself was the manager of the powder works of the French Government just before the revolution of 1789.

Chapter 33

Explosives

Explosives serve two main purposes. In times of peace, they serve as a life-saving device in dislodging rocks, coal, and other minerals; in times of emergency, they serve for national defense against an enemy. As to their use, the day may be approaching when all disputes will be settled on their merits, by court or council. It is proper in the meantime for the Government to provide the necessary explosives for the protection of persons, property, and institutions within the national boundary. In a war emergency, such as the present one, it is the young men who quickly learn the operation of the explosives manufacturing plants; it is astounding how skillfully they discharge their duties. When the day of universal peace arrives, however, explosives will continue to be manufactured, for as man's servant in the discharge of physical tasks, they have become indispensable. As an illustration of the advantages which explosives confer, the following may be cited. It took 30,000 men 11 years to build a 3-mile tunnel for a Roman aqueduct system; the same construction by means of modern machinery and explosives requires only 100 men working 10 months.

An explosive is a chemical substance or a mixture of substances which, when struck with a hammer or touched by a flame or electric spark, is suddenly changed with the formation of gases and the simultaneous development of heat. If this rearrangement takes place inside a closed chamber, its walls are shattered. The substances which serve as useful explosives are completely inert, for they must be manufactured, handled, and transported without a premature explosion. The extremely sensitive substances such as silver tri-iodide, which explode at the touch of a feather, have no value as commercial explosives. Among the useful explosives a distinction is made on the basis of sensitivity, but of shattering power; nitroglycerin is a very sensitive high explosive; picric acid, an insensitive one. Very sensitive substances such as mercury fulminate and lead azide are used as primers, that is, to start the explosion of a less-sensitive substance, which a heavy blow would not set off. A list of the more important explosives is given in Table 81.

The explosives listed in Table 81 are not exclusive in every case; thus dynamite is used in war to damage bridges and railroad tracks, in order to hamper the pursuing enemy. Smokeless powder is used in the small amount of fine ammunition consumed by hunters. Black powder is used in various types of military shells, and as the igniter charge in primers. There are other substances which are of importance in the explosive

TABLE 81.—*Uses of the more important explosives.*

Dynamites (nitroglycerin with wood meal, nitrates, or kieselguhr)	high explosive for peace
Blasting gelatin (nitroglycerin 90% and nitrocellulose 10%)	high explosive for peace
TNT (trinitrotoluene)	high explosive for war use
Picric acid	high explosive for war use
Ammonium nitrate	high explosive for war use
Smokeless powder (nitrated cellulose gelatinized by acetone, in grains or sticks)	mild explosive for war use
Black powder	mild explosive for peace use and war use
Mercury fulminate	auxiliary explosive, war use
Lead azide	auxiliary explosive, war use

industry for various purposes. Diphenylamine and urea are stabilizers for smokeless powder. Dynamite may contain anti-freezing agents.

PROPERTIES AND TESTS

The shattering power, also called the brisance, of an explosive depends upon two properties, the strength of the detonation, and the velocity of propagation of the explosion within the explosive itself. The strength depends upon the volume of gases developed, and upon the amount of heat liberated. It is measured by performing the explosion of a known weight of the substance within the cavity of a lead block; the cavity is distorted by the action. The volume of the distended cavity is a measure of the strength of the explosion (Trauzl test). Another method is the ball gun, a 500-pound mortar suspended as a pendulum, which shoots a 36-pound shot; the recoil of the mortar is measured. The two methods give concordant results.

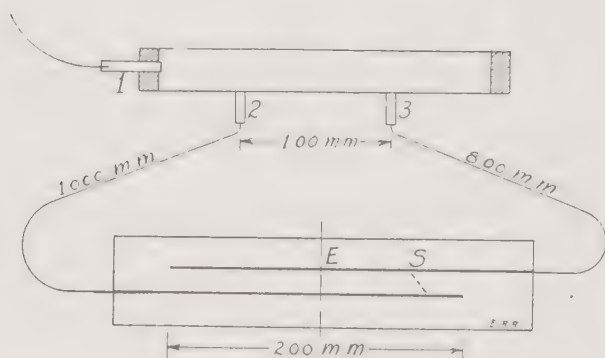


FIGURE 193.—Dautriche method for velocity of detonation; 1, main fuse; 2 and 3, detecting fuses. The distance *E-S* is measured.

The velocity of detonation or explosion is determined by the method of Dautriche. A tube filled with the sample is fitted with two auxiliary detonators, which are set off when the explosion passes them; each is connected to a standard trinitrotoluene fuse (copper pipe) which terminates at a thick sheet of lead (3" × 15" × 1/2"), as indicated in Figure 193. The first fuse, on burning, causes a bend in the sheet; the position of the point where

velocity of detonation relative to E is the measure of the velocity.¹ Some data for strength and velocity of explosion are given in Table 82.² The velocity of detonation depends mainly upon the chemical constitution, but very appreciably upon the density of the explosive, raised by compression; the denser it is, the higher the velocity; thus for picric acid, it may be raised from 5000 to 7000 meters per second.

TABLE 82.—Strength and velocity of explosion.

	Strength by Ballistic Gun	Velocity in Meters per Second
Nitroglycerin	14.0
Ammonium nitrate 80%, TNT 20%	12.1	5920
Trinitrophenyl	12.1*
Nitrocellulose, 13.35–13.50% N	12.0	6383 (d. 1.25)
Picric acid	10.6	8183 (d. 1.55)
Ammonium nitrate	10.5
TNT (trinitrotoluene), the standard	10	7600
Dynamite, 50% nitroglycerin	9.8
Black powder	300 (d. 1.04)

* Usually higher than the maximum rate for TNT.

The sensitiveness of explosives is measured by dropping a weight from various heights; the greater the height required to cause explosion, the less sensitive is the substance. The stability on storage is determined by measuring the time and temperature required to evolve fumes of nitrogen dioxide (NO_2), and in other ways. Of great importance is the uniformity of the commercial brand, so that results may be calculated beforehand, and duplicated by using the same weight of the same material.

Explosives intended for use in coal mines in which there is fire-damp (methane, CH_4), which forms explosive mixtures with air, are tested by burning them in a long gallery resembling a smoke-stack laid on its side, in which the conditions in the mine are reproduced. Those which fail to explode, or the gas mixtures are placed on the permissible list of the Bureau of Mines.³ Such explosives have short flames of short duration; their velocity of detonation is about 3000 meters per seconds.³ Their detonation velocity is reduced by a proper choice of ingredients, and particularly by the addition of water in the form of crystal water or admixed materials; temperature reduction does not materially affect their strength.

In general the duration of the flame is inversely proportional to the velocity of detonation. Secondary flames, due to evolved gases which are combustible (CO), are repressed by the addition of alkaline salts. The height and length of flame are studied by photography. The following table will indicate the time and size: gunpowder (black), duration 0.077 second, length 110 mm. (for 100 grams); gun-cotton (nitrocellulose mixture), 0.0013 second, 97 mm. (for the same weight). Ammonium nitrate and picric acid show much shorter flames.

¹ "Explosives, their history, manufacture, properties and tests." A. Marshall, Philadelphia, P. Blakely & Co., 2d ed., 1932.

² "Strength and velocity of detonation of various military explosives," W. C. Cope, *Ind. Eng. Chem.*, 12, 870 (1920), and from p. 307, "High explosives," by Colver, London, Crosby Lockwood & Co., 1918.

³ "Permissible explosives, mining equipment, and apparatus approved prior to January 1, 1923." U. S. Bureau of Mines, *Bur. Mines Tech. Paper No. 333*.

The pressure developed by the explosion of a nitrocellulose in a gun chamber is about 3 tons per square inch.

EXPLOSIVES FOR WAR

The military explosives for artillery fall into two classes: the propellant, which fills the cartridge and serves to force out the shell with a high velocity, and the bursting charge, carried by the shell, which shatters it after it has traveled a definite distance. For small arms ammunition, such as pistols and semi-automatic rifles, the cartridge contains the propellant which drives out the bullet, which may be for example lead in a jacket composed of a zinc copper alloy. Anti-tank rifles shoot sharp nosed solid steel bullets. The hand grenade has no propellant; it contains only a bursting charge, and it is propelled by hand.

The propelling charge is a mild explosive; its velocity of detonation is relatively low; its function is to exert a sustained pressure on the shell, forcing it to take the rifling of the gun bore, and continuing in effect until the shell is free from the gun. Nitrocellulose in fibre form is a high explosive; but gelatinized, so that its surface is greatly reduced, it becomes a mild explosive. Its rate of burning is regulated further by its shape, diameter, length, and perforations of the sticks into which it is formed; it is the propellant generally used, with or without certain additives. For a 3-inch (diameter) shell, the cartridge is about 1 foot long, made of cold-drawn brass; the shell also is about 1 foot over all. In order to force the propelling charge, a hammer blow ignites a small fulminate cap forming part of the primer, which contains a sizable amount of black powder; this explodes in turn, and flashes into the propellant. The primer is 1 inch in diameter, and is threaded into the thick base of the cartridge. The shell is crimped into the cartridge, surmounting it, and the two form one piece which, after being filled, is moved about as a unit.⁵

The shell may contain only the high explosive, such as TNT, or TNT mixed with ammonium nitrate (Amatol), or picric acid or its salts; its only function is to travel to the desired point and there be shattered into fast-moving fragments which become the actual missiles. The shell may also contain, besides the bursting charge, somewhat reduced, balls packed in a shell of rosin or black powder; it is then a shrapnel shell.⁶ Finally it may contain a war gas instead of the balls.⁷ The shell is ignited by a fuse whose length is adjusted by the relative lengths of a horizontal fuse in a ring, which may be turned a part or all of a circle, to a canal leading the flame to a black powder charge, which in turn flashes the high explosive; the first fuse is ignited automatically as the shell emerges from the gun. The shell is supplied with a heavy base and often an aluminium nose piece.

⁴ The rifling of the gun consists of grooves; the shell has a band of copper which is wedged into the body of the shell; the soft copper is forced into the wide grooves and "takes" the rifling; the grooves are curves, and as the shell progresses, it acquires a rotational motion which permits a more accurate and truer trajectory.

⁵ During 1915, the unfilled 3-inch shell and cartridge sold to a foreign government for \$14. The war was in progress the cost of smokeless powder to the government was dropped from 50¢ a pound to 44 cents.

⁶ Named after Lieutenant Shrapnel, the inventor.

⁷ Chapter 34.

⁸ The length of the horizontal, adjustable fuse controls the time of burning before explosion; the distance the shell travels before it bursts. Instead of a time fuse, some shells have percussion caps, set off as the shell strikes an obstacle.

NITROCELLULOSE

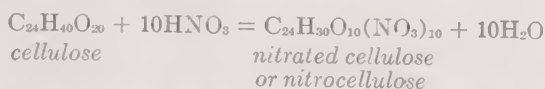
The introduction of nitrocellulose as a military explosive became possible through the labor of the British scientist, Abel, who showed that the removal of impurities would permit the production of a material of reproducible properties, and relatively safe to handle.

The cotton waste is cleaned by hand, and carded to a fluffy open mass; it is dried by warm air, and the cotton is then cooled in closed boxes, to prevent reabsorption of moisture (the moisture content is 1 per cent or less). The nitration was formerly performed in pound lots, in earthenware pans, for a period of 24 hours after a preliminary 3-minute dip; the product was then centrifuged and washed. The nitration is now performed in the pans themselves, so that no transfer is needed in order to free the cotton from the excess acid. Still another way is the direct displacement method, in which the acid after action is displaced by cold water run quietly through a rubber hose, while the spent acid is drawn off at a corresponding rate from the base of the pan. The water forms a lower layer; as more is passed in, the cotton loses adhering acid.

The composition of the mixed acid for the nitration is not far from the following figures: 71 per cent H_2SO_4 , 21 per cent HNO_3 , 7.5 per cent H_2O , 0.5 per cent HNO_2 impurity.

In the displacement method, 20 pounds of cotton per pan are nitrated with 60 pounds of mixed acid, which is more than is used in the older pot method, but the time is shorter, $2\frac{1}{2}$ hours against 24 hours. The nitrated cotton is next boiled with several changes of water for 10 periods, which run from 12 hours, the first, to 2 hours, the last; this boiling with water is the previous practice of using a dilute caustic solution. The boiling is followed by shredding and reduction to short lengths of fiber in a mangle engine, as used in paper plants.⁹ After draining, the wet pulp is best cut into short rods which are dried in a warm closet. Until shredded and beaten, the cotton retains its original appearance; it is somewhat more pliant and, unlike the original material, it is soluble in potassium hydroxide solution.

The standard military powder in the United States requires a nitrocellulose which contains 12.8 per cent nitrogen on analysis, which agrees with the formula $\text{C}_{24}\text{H}_{30}\text{O}_{10}(\text{NO}_3)_{10}$; the equation is



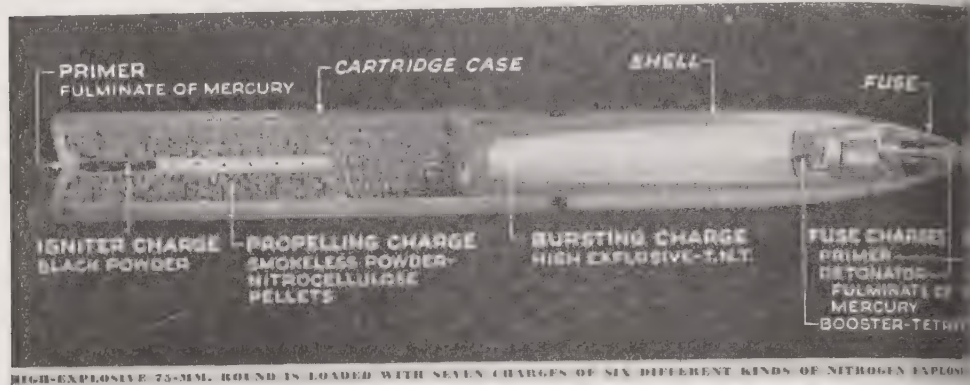
The water formed is bound by sulfuric acid present and does not hinder the reaction.¹⁰

In the preparation of the smokeless powder (U. S.), the nitrocellulose is treated with alcohol in the first step; another procedure is to treat the pressed pulp from the beaters with several changes of alcohol, thus avoiding the beating operation. Ether is next incorporated in a mixing machine with a cooled jacket; a small amount of diphenylamine is added also, as a

interferer 21.

The name "nitrated cellulose" is correct, while "nitrocellulose" is incorrect, but the distinction is rather unimportant as the name is too well established in several industries to make a change advisable.

stabilizer. The proportions are: 84 pounds nitrocotton, 26.4 pounds alcohol, 3.6 of water, 48.4 of ether, and 0.38 of diphenylamine.¹¹ The soft is sieved free from coarse grains, and forced through a die into rods of various diameters, which are made into lengths, as desired, by an automatic cutter. The die also introduces longitudinal perforations in the grain, and is larger in large grains. The outside of the grain is now also fluted, and is larger in large grains. The outside of the grain is now also fluted all for the purpose of increasing the burning surface as the shell travels outward, creating a larger chamber to be filled with the gas. The translucent jelly-like grains are freed from the solvents, ether and alcohol, in drying-rooms with fans, after which they are dry and hard. The recovery of the solvent vapors diluted with air is not always undertaken. Smokeless powder deteriorates with time, and must be tested at intervals.



HIGH-EXPLOSIVE 75-MM. ROUND IS LOADED WITH SEVEN CHARGES OF SIX DIFFERENT KINDS OF NITROGEN EXPLOSIVES.

FIGURE 194.—High-explosive 75-millimeter round is loaded with seven charges of different kinds of nitrogen explosives, all shown in this picture. (Reproduced from *Life* for March 23, 1942, page 73.)

Cordite¹² is a "double base" powder; it contains nitrocellulose and nitroglycerin. In one of its formulas, Cordite M.D., there is nitrocellulose 65 pounds, nitroglycerin 30 pounds, mineral jelly 0.5 pound; in another formula, Cordite B., there is nitrocellulose 37 pounds, nitroglycerin 58 of nitroglycerin, and the same amount of mineral jelly as stabilizer. The gelatinizing agent is acetone, which may be recovered from the drying-room vapors by absorption in sodium bisulfite. There are many other smokeless powders with nitrocellulose as base, with modified formulas, used by the various nations. Nitrocellulose itself generates on explosion carbon monoxide in addition to other gases¹³; by the addition of an oxidizer such as potassium nitrate, the poisonous and combustible carbon monoxide is changed to harmless carbon dioxide. Smokeless powder charges for large guns are preferably packed in silk bags.

Nitrocellulose is used for other purposes than explosives; the degree of nitration is less, just sufficient to render the cellulose soluble in ether, for example. Cotton is not always chosen for these less nitrated materials; it may be replaced by wood pulp.¹⁴

¹¹ Formula and preparation will be found in Chapter 27.

¹² The British standard smokeless powder.

¹³ The complete analysis is: CO 28.5 per cent; CO₂ 19.1; CH₄ 11.2; NO 8.8; N₂ 8.6; H₂O 2.0.

¹⁴ Products from lower-nitrated cellulose in Chapter 35.

PICRIC ACID AND TNT

ric acid, symmetrical trinitrophenol, $1\text{-OH-2,4,6-(NO}_2\text{)}_3\text{.C}_6\text{H}_2$, is a white solid with melting point 121°C . It is made by the nitration of phenol which has previously been treated with sulfuric acid to form phenol sulfate; to the 50 per cent solution of the sulfonated phenol, placed in a number of earthenware pots, 65 per cent nitric acid is added at a very slow rate. The temperature rises and remains elevated for some time while the pots are packed in sand; the reaction proceeds to its end, after which the pots cool. The picric acid separates in the form of yellow crystals; the spent acid is run off, and the crystals washed in large volumes of water, filtered, and dried at a moderate temperature. The formation of lead picrate must be avoided, for it is 5 times more sensitive than picric acid. Pure picric acid may be packed into shells or it may be melted with an inert substance which lowers the melting point considerably; the lower temperature is safer.¹⁵ Picric acid may also be made by the action of potassium nitrate and sulfuric acid on phenol.

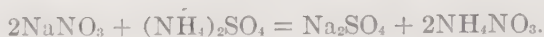
Nitrotoluene, TNT, $1\text{-CH}_3\text{-2,4,6-(NO}_2\text{)}_3\text{.C}_6\text{H}_2$, has about the same explosive properties as picric acid, but possesses a lower melting point (80°C), and is free of acid properties; this is an important advantage. Dangerous metallic derivatives cannot form. The nitration is performed in three steps, in a steel vessel equipped with an agitator and coils which may receive steam for heating or water for cooling. First the mononitrotoluene is made with the use of a mixed acid containing 60 per cent sulfuric, 14 per cent nitric, the balance water. As the mixed acid is introduced it displaces a cycle acid which is saved and re-used. The "mono oil" is pumped over to the bi-nitrator, and nitrated to the "bi" by the use of a mixed acid containing 67 per cent sulfuric and 16 per cent nitric. In the same nitrator there are placed: a charge of oleum, then a charge of mononitrotoluene, 40 parts sulfuric and 60 parts nitric, which mixes with the mononitrotoluene; the mixture acts on the "bi" oil, producing the final material, trinitrotoluene. The strength of the mixed acid and its proportion of nitric acid rises from the "mono" mix to the "tri" mix; the temperature also is higher at each succeeding step. The period of cooking varies; thus in one plant, 30 minutes for the "mono," 5 or 10 minutes for the "bi," 30 minutes for the "tri"; after adding the acid and drawing off the spent acid, and settling, is added. The spent acid from the "tri" is fortified by addition of 62 per cent sulfuric acid and becomes the "bi mix"; the spent acid from the "bi" is fortified to become the "mono mix." The "mono" waste acid is of no further use; it is nitrated, and its sulfuric acid residue concentrated. All sulfuric acid recovered and used again, part of it being returned to the oleum plant. Mononitrotoluene is washed, treated with Sellite (sodium sulfite solution), washed again, dried by blowing warm air through the melted body, and pressed. It forms pale yellow flakes. For loading shells, the TNT is melted in a shell-filling station, and poured in. On exploding, some free carbon is produced which causes a black cloud.¹⁶

1 part picric acid and 1 part nitronaphthalene mixed melt at 49°C .
complete analysis is: CO_2 3.7 per cent; CO 70; N_2 20; H_2 1.7; C 4.

The quality of the product is judged by its setting point; for U. S. government specifications grade 1, it must be 80.2°C .

Tetryl is trinitrophenylmethylnitramine, $\text{C}_6\text{H}_2(\text{NO}_2)_3\text{N} \cdot (\text{CH}_2)_3\text{NO}_2$, a yellow powder, and is made by the nitration of dimethylaniline. Tetrazyl is a booster explosive and is the standard bursting charge for anti-air guns (up to 40 mm.); it is a high explosive, with an expansion higher than that of TNT. (Hexyl is hexanitrodiphenylamine, also a yellow powder.) Explosive D is ammonium picrate, an orange powder.)

Ammonium nitrate is mixed with TNT in order to lower the cost, also as an oxidizer; by itself it can be detonated only with difficulty. mixed with TNT, the mixture is stronger than pure TNT, and is easily detonated. Ammonium nitrate is made by adding sodium nitrate to a solution of ammonium sulfate; sodium sulfate separates out, for the greater part; the ammonium nitrate¹⁷ is crystallized from the slightly dilute liquor:



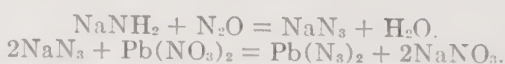
Ammonium nitrate is also made from odds and ends of nitric acid neutralizing with ammonia.

Potassium chlorate, KClO_3 , and perchlorate, KClO_4 , form the basis of some high explosives, usually containing 75 per cent chlorate, 15 per cent dinitronaphthalene, some other suitable nitro derivative, and 6 per cent castor oil to reduce the sensitiveness to a safe limit.

Nitroguanidine, $\text{NH}_2 \cdot \text{C} : (\text{NH}) \cdot \text{NH} \cdot \text{NO}_2$, obtained, for example, by dissolving guanidine nitrate in concentrated sulfuric acid, and then diluting, has been used as an explosive. A flashless powder (reported by Guinot) contained 50 per cent ammonium perchlorate, 40 per cent nitroguanidine, and 10 per cent pitch. There are countless other explosive mixtures, with a variety of names, many of which are patented.

The propellant charge of the cartridge is detonated by means of a sensitive mixture, such as 85 per cent fulminate of mercury, $\text{Hg}(\text{CNO})_2$; 15 per cent potassium chlorate, with or without powdered glass; still more may also be added. In the 3-inch shell and in larger sizes, the fulminate cap flashes into the main priming charge, black powder, which in turn ignites the propellant. The fulminate is made by dissolving mercury in 60 per cent HNO_3 , and adding alcohol to the solution; the fulminate forms with evolution of heat, and separates as a gray powder, which must be washed and dried at a low temperature. Fulminate is as sensitive as nitroglycerin, twice as sensitive as nitrocellulose, and 11 times as sensitive as TNT.

Lead azide may be substituted for mercury fulminate. It is made by the action of sodium azide on lead nitrate in solution; by adding dextrin to the lead solution a yellow-white powder, 90 to 95 per cent pure, is formed, which is safer to handle. It is stored saturated with water. Lead azide is half as sensitive to shock as fulminate.



¹⁷ "Effecting and controlling crystallization of ammonium nitrate," J. Ester, *Boll. Soc. Chim. Engg.*, 20, 401 (1919).

INDUSTRIAL EXPLOSIVES

pe explosives used for peace-time purposes, the industrial explosives, chiefly dynamite, a high explosive, black powder, a mild explosive, and explosives, such as the ammonium nitrate mixtures.¹⁸

These might be added nitrostarch, a slightly yellow powder, made by mixing starch with mixed acid.¹⁹ Liquid oxygen²⁰ with charcoal is also an industrial explosive. The characteristics of the permissible explosives have been given in the introductory paragraphs.

The mining industries consume about 75 per cent of the industrial explosives produced; coal mining requires about 80 per cent of the black powder and permissible explosives.

Nitroglycerin and Dynamites. Nitroglycerin is made by nitrating glycerin; by itself it is too sensitive; it was in an effort to reduce its sensitivity that Nobel discovered dynamite, a solid, made by absorbing the nitroglycerin in kieselguhr, a diatomaceous earth. Since then, other methods have been developed; in America, the dynamites do not contain kieselguhr but mainly wood meal, with sodium nitrate addition. The strength of dynamite depends mainly on the content of nitroglycerin; 75 per cent is the highest; other grades have 20, 40, and 60 per cent. Special grades are made to specifications. The effect of the wood meal (or kieselguhr) is to make the dynamite, so that ordinary transportation shocks do not destroy it; it is packed in parchment paper "cartridges," not in metal boxes, for the same reason. The cartridges are packed in sawdust in wooden boxes, and one of these boxes dropped from a height on rocks below will explode.

A very pure grade of glycerin²¹ is used. The mixed acid for the nitration is, in the latest procedures, 50 per cent sulfuric acid and 50 per cent nitric acid, hence it is anhydrous. The nitrator is a steel vessel with agitator and cooling coils similar to the nitrator used for TNT described earlier in this chapter. The cooling is by brine, and the temperature is kept at 2 to 5°C. below the melting point of the dry product. The batch is 1100 lb. of glycerin, and five times this weight of mixed acid. The spent acid may run 73 per cent sulfuric acid, 10 per cent nitric acid, and 17 per cent water. The time is one hour; the reaction is $C_3H_5(OH)_3 + 3HNO_3 \rightarrow C_3H_5(NO_3)_3 + 3H_2O$. The product is washed with several waters, then soda ash, and again with water; finally it is run through a mat of burlap to remove water droplets and is then ready to be mixed with wood meal, kieselguhr, or nitrocellulose. The product is about 2.3 times as powerful as glycerin taken, compared with the theoretical 2.467 times.

The spent acid must be diluted slightly to prevent after-nitration of the glycerin remaining in solution. For ordinary dynamite, the wood meal and sodium nitrate are weighed into rubber bags, and to each the weighed amount of nitroglycerin is added and mixed by hand. The mixture is sieved and packed into parchmentized paper by an automatic filling machine. Black meal dynamite is yellow and looks slightly wet.

Sample: Ammonium nitrate 60 per cent, TNT 15 per cent, aluminum powder 18 per cent, charcoal 7 per cent.

Mines Bull. No. 219, 88 (1923).

Liquid oxygen explosives," G. St. J. Perrot and N. A. Tolch, *Bur. Mines Bull.* No. 349 (1932).

Chapter 32.

A dynamite cartridge may be fired by an electrical spark, passed to a copper detonating cap which is slipped into the paper covering; this explodes a priming mixture bead similar to a match head; this in turn explodes a small store of fulminate in the copper capsule, which then sets off the dynamite.

Nitroglycerin solidifies at 13°C .; frozen nitroglycerin is difficult to handle, and the operation of thawing it, with haphazard equipment, is dangerous. A non-freezable dynamite is therefore made by mixing 20 parts of glycerin dinitromonochlorhydrin,²² which remains liquid at -30°C . with 80 parts of nitroglycerin.

Recently ethylene glycol, $\text{CH}_2\text{OH} \cdot \text{CH}_2\text{OH}$, made from ethylene, has been nitrated on the large scale and successfully introduced in the explosive industry (Chapter 25).

Black Powder. Black powder, often called gunpowder, is no longer a military propellant, for it is too weak, and it develops a cloud of smoke. Its products of decomposition are 44 per cent gaseous and 56 per cent fine divided solids.²³ It is mainly an industrial explosive now, for coal mining, particularly, but it still renders service in military explosives: in the primer for rapid-firing artillery and navy guns, as the intermediate explosive between the fulminate and the main charge of smokeless powder; in the fuse of explosive shells as a time fuse, and in shrapnel shells. In coal mining it is the main charge, and also forms the core of the fuse.

TABLE 83.—*Production of peace-time explosives in the United States in 1935.*

	Pounds	Value in cents per pound
Dynamite	257,326,065	10.4
Permissible explosives	76,438,168	10.4
Nitroglycerin	347,328	20.0
made and consumed in shooting oil wells	1,703,791	...
Blasting powder	29,440,225	6.0
Pellet powder	26,670,405	6.0
Gunpowder, black and smokeless, 1935.....	28,215,211	16.5

* Bureau of the Census.

Black powder of standard composition contains 75 per cent potassium nitrate, 15 per cent charcoal, and 10 per cent sulfur; in the United States sodium nitrate is substituted for the potassium salt, in about the same percentage. The three ingredients are powdered separately, then mixed together in an edge runner,²⁴ with the addition of a little water; the mass is then compressed, granulated, and sieved. The blasting cartridge is a cylindrical piece formed by pressing, with one perforation (in the longitudinal axis).

OTHER PATENTS

1,849,356, an explosive nitrocellulose grain surface treated with tetraminonitrate; 1,775,271, a nitroglycerin cell, container for charge in shooting wells; 1,814,980, process of manufacture of TNT; 1,868,388, on diethylglycol dinitrate (A. Hough); 1,828,788, method of explosives of the dynamite and gelatin type; 1,820,567-S, explosives consisting of

²² $\text{CH}_2\text{Cl} \cdot \text{CH}(\text{NO}_2) \cdot \text{CH}_2(\text{NO}_2)$, made by nitrating glycerin monochlorohydrin, $\text{CH}_2\text{Cl} \cdot \text{CH}_2 \cdot \text{CH}_2(\text{OH})$.

²³ The solids are K_2CO_3 or Na_2CO_3 about 60 per cent; sulfate about 15 per cent; sulfide about 10 per cent; and sulfur.

²⁴ Chapter 44.

chlorate, sodium nitrate, TNT, ortho-nitrotoluene and sawdust; LS19.457 of making a colloidal starch explosive

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In the present titanic war struggle, there has been reported only one established and sustained use of war gas, and that one by the Japanese against Chinese cities. While fervently hoping that the actions of the enemy will not force the United Nations to employ in their turn this deadly weapon, it would be criminal for the organized forces of our country not to prepare for such an event, by laying up stocks of gases, by working out new ones, and perfecting the manufacture of the older ones. Similarly, on defense, it is but our duty to design, prepare and distribute to the armed forces as well as to the armed forces devices for the protection against war gases and methods for decontamination.

Chapter 34

Chemical Factors Other than Explosives in Warfare*

The use of poison gases by the German army at Ypres on April 22, 1915, during the first World War, marked a new era in modern warfare. Popular opinion is that this form of warfare was original with the Germans; such, however, is not the case. In milder form, chemicals have been used in warfare for many centuries. The first recorded effort to overcome an enemy by the generation of poisonous and suffocating gases seems to have been the wars of the Athenians and Spartans (431-404 B. C.) when the latter besieged the cities of Platea and Belium. The attackers saturated the walls with pitch and sulfur and burned it under the walls of these cities in hope of choking the defenders and rendering the assault less difficult. Similar uses of choking and poisonous gases are recorded in the history of the Middle Ages.

In the attack of April 22, 1915, the German army made use of chlorine discharged from stationary steel cylinders; the cloud of chlorine gas was carried along by the wind. It was found that a cloth bandage steeped in sodium thiosulfate (hypo¹), and wrapped over the nose and mouth, gave fair protection against chlorine. These bandages do not protect the eyes, so that when the enemy sent over tear gases or lachrymators in shells, no damage was done. The lachrymators are used in shells because they are liquids at ordinary temperature and do not pass into vapor form rapidly enough to be used in cylinders. In chemical warfare parlance the word "gas" is used in a broad sense, and denotes any substance, solid, liquid, or gas, which is dispersed in the air and which irritates the lungs, eyes, or skin. Protection against tear gases was given by hoods with eye-pieces; the hoods could be impregnated with suitable chemicals; later, respirators were developed.

The gas used by the German army from April to June, 1915, was commercial chlorine, but in December of that year, a mixture of chlorine and phosgene was introduced. Phosgene is seven times as toxic as chlorine.

* In collaboration with Major-General Amos A. Fries, U. S. A., former Chief of Chemical Warfare Service, Washington, D. C.

¹ Chapter 4

to neutralize, and has a delayed action which makes it still more
 ivo. To absorb phosgene, the British hoods and the first French masks
 impregnated with a solution of sodium phenolate and hexamethylene-
 mine. The British changed after a time from the hood or helmet, as it
 called, to an impervious mask with a box respirator (canister) attached.
 The next development in the offense was the use of chloropicrin in shells.
 scattered their liquid charge by the explosion of the "booster."
 picrin, CCl_3NO_2 , is a liquid boiling at 112°C ., much less toxic than
 gene, but distinctly lachrymatory. It causes vomiting; this effect
 is it difficult for the soldier to keep on his mask.

In July, 1917, the German army began using mustard gas, a liquid boil-
 t 219.5° to 228°C ., which attacks the skin as well as the lungs and
 causing bad burns which may incapacitate a soldier for a number of
 s. While the mask protects the face satisfactorily, the problem of pro-
 g the whole body is a serious one. Special ointments and special
 ing were devised at once, but were not really satisfactory at the time
 armistice was signed.

Another type of chemical agent of importance in warfare is the so-called
 e gas, diphenylchloroarsine. This is a high-melting solid which is dis-
 d as a very fine smoke or dust by means of high explosives. In order
 tect satisfactorily against this toxic smoke, special filtering pads are
 oyed.

It was also found that toxic smokes could be more effectively dispersed
 at; this is accomplished by mixing substances such as diphenylchloro-
 with smokeless powder and igniting with suitable starting and match-
 compositions.

In the present war there has been no use of gas in Europe, and no new
 erefore has come to the attention of the public (June 6, 1942.)

CLASSIFICATION

The various chemical agents employed for the production of casualties
 be classified according to their physical properties, their tactical use, or
 physiological effects. It has already been stated that chemical war-
 agents may be solids, liquids, or gases at ordinary temperature. Depend-
 on physical condition and physical constants, particularly the vapor
 ure, chemical warfare materials are also classified as persistent and
 persistent. Gases in general are non-persistent, but liquids and solids
 ot to be persistent, because of their slow volatilization. Thus chlorine
 phosgene are non-persistent, as they volatilize quickly; however, chloro-
 , a liquid even at summer temperatures, is more persistent. Mustard
 as a still higher boiling point and is highly persistent; and the solid
 ance chloroacetophenone will persist for weeks or months. Solids that
 become vaporized as smokes behave like gases and are relatively
 persistent.

The tactical use of chemical warfare materials is largely governed by this
 erty of persistency. Thus non-persistent chemical agents such as phos-
 are employed against positions to be attacked shortly afterward, where-

as persistent chemical agents such as mustard gas are employed to hold the enemy or to render positions untenable.

The chemical agents are classified physiologically as follows:

- (a) Agents which produce their effects through inhalation:
 - (1) Asphyxiants and respiratory irritants such as phosgene and mustard gas.
 - (2) Nauseating gases: Diphenylchloroarsine, or chloropierin.
- (b) Lachrymators or tear gases: Bromobenzyl-cyanide or chloroacetophenone.
- (c) Vesicants or skin-blistering agents: Mustard gas.

In many instances a single chemical agent may be capable of producing a number of different physiological effects; thus, mustard gas is classed as an irritant and as a vesicant; to some extent it is also a lachrymator, as are most of the chemical agents which produce physiological effects.

TABLE 84.—*Casualty-producing chemical agents.*

Chemical Agent	B. pt. ° C.	Physical State	Physiological Action*	Method of Projection
Chlorine (Cl_2)	-33.6	Gas	l,ri	Cylinders
Phosgene (COCl_2)	8.2	Gas	l,ri	Cylinders, shell, bombs
Chloropierin (CCl_3NO_2)	112.0	Liquid	ri,tg,e	Shell
Superpalite (CCl_3COCl)	128	Liquid	l,ri	Shell
Mustard gas ($\text{CH}_2\text{Cl} \cdot \text{CH}_2$) ₂ S.	219.5	Liquid	l,ri,v	Shell, bombs
Lewisite ($\text{CHCl} : \text{CHAsCl}_2$)	190	Liquid	l,ri,v	Shell
Bromoacetone ($\text{CH}_3\text{BrCOCH}_3$)	126	Liquid	lach,tg	Shell, bombs
Diphosgene (ClCOOCCl_2)	...	Liquid	ri,l	Shell
Bromobenzyl-cyanide ($\text{C}_6\text{H}_5\text{CHBrCN}$)	242	Liquid	lach	Shell, bombs
Chloroacetophenone ($\text{C}_6\text{H}_5\text{CO} \cdot \text{CH}_2\text{Cl}$)	247	Solid	lach	Shell, candles, grenades
Diphenylchloroarsine (C_6H_5) ₂ AsCl	383	Solid	i,e	Candles, shell

* l = lethal, ri = respiratory irritant, i = irritant, e = emetic, tg = tear gas, v = vesicant, = lachrymator.

Table 84 lists the more important chemical agents employed in World War for the production of casualties and also gives for each some of the physical properties, physiological effects, and the type of container (shell or bombs) used for their dispersion. It will be noted that all chemical agents listed contain either chlorine or bromine, so that it appears probable that one or more halogen atoms are necessary in casualty-producing chemical agents.² Practically all these chemical agents can be loaded into steel projectors or containers without danger of corrosion, except the bromine compounds, which attack steel; shells lined with lead or enameled must then be used. It was to avoid the special lining that a suitable substitute for bromobenzyl-cyanide was sought. As a result of this search chloroacetophenone was discovered; it does not attack steel and is as effective a lachrymator as bromobenzylcyanide.

Medical Aspects. All the casualty-producing chemical agents are lethal in sufficiently high concentrations, but it is difficult to reach such concentrations in the open; many of them, however, produce light casualties in very low concentrations and it is for this reason that chemical agents have been found to be so effective in warfare. That the casualties

² Hydrocyanic acid gas, or hydrogen cyanide, HCN, is an exception; it was not found effective in the field, however, because it dissipated too rapidly.



FIGURE 195.—Two airplanes laying a smoke curtain around a bombing target. (Courtesy of the U. S. Army Air Corps.)

mainly light was clearly brought out by the report of the Surgeon General of the United States Army in 1920, which shows that 27.3 per cent of all United States Army casualties during the World War were gas casualties, but all except 2 per cent of these were temporary casualties and recovered. On the other hand, approximately 25 per cent of all casualties produced by weapons other than gas failed to recover. It follows that a man who is injured by gas had twelve times as many chances for recovery as the man who had been injured by shell fire, bullet, or bayonet.

The chemicals used in chemical warfare injure by direct irritant and burning action to the skin and mucous membranes with which they come into contact. Such chemicals are powerful germicides, and as a result, a wound is sterile. Some of the warfare chemicals have a pronounced irritant action on the mucous membrane of the upper respiratory tract, yet have little effect on the lungs proper. Others have only a light irritant action on the respiratory tract, but have a strong burning effect on the lungs; still others possess irritant and burning properties in nearly equal degree. For these reasons, contrary to wide-spread belief, there are few after-effects among those wounded by gas or chemicals, provided they had ordinary body resistance.

SMOKE SCREENS

In addition to the production of casualties, chemical agents are also extensively employed for producing smoke screens, incendiary effects, and in gas-mask canisters for the adsorption of the casualty-producing agent.

A most effective smoke-producing chemical is white phosphorus, which ignites spontaneously in contact with air, producing a dense white smoke. Phosphorus for this purpose is used in shells, grenades, or bombs. Other important smoke-producing materials are sulfur trioxide in the form of oleum, stannic chloride, and titanium tetrachloride; these three chemical agents produce white smoke as a result of contact with the moisture in the atmosphere. They were employed in shells and grenades. Since 1914 titanium tetrachloride has come into extensive use for the production of screening smokes sprinkled from airplanes. Still other important smoke materials were the zinc-containing mixtures which were used in a smoke box in smoke candles and in certain of the smoke grenades. One such mixture has the composition:

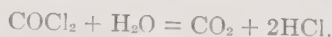
Zinc	34.6 per cent
Carbon tetrachloride	40.8
Sodium chlorate	9.3
Ammonium chloride	7.0
Magnesium carbonate	8.3

This mixture when ignited produces a light gray smoke of high obscuring power. A smoke box dropped behind a fleeing vessel burns for 9 minutes. The H C Mixture is zinc and hexachloroethane.

Various chemicals were employed during the war of 1914-18 as incendiaries chiefly in the form of airplane bombs; one type contained thermite, a mixture of aluminum powder and iron oxide, surrounded by oil set to jelly with a small amount of soap; another type contained white phosphorus (Chapter 7) in fuel oil, which provides for spontaneous combustion on contact.

with air. In the present war, incendiary bombs of two types chiefly been employed: the scatter bomb and the intensive bomb. The scatter bomb carries an explosive charge which scatters the load of oil, or oil-phosphorus. The intensive bomb is most generally of magnesium, with a charge of thermite. It has two stages of burning; in the first, molten iron is poured through appropriate openings; in the second, the magnesium case burns. It may be extinguished by covering it with sand, salt, or commercial powder. A spray of water will hasten the burning.³

The chemicals employed in the gas-mask canister are charcoal and soda. The charcoal is an especially activated product prepared from nut shells. It adsorbs practically all gases to some extent but is specially active in the adsorption of the vapors from liquids. It acts catalytically also; for phosgene which is decomposed by water vapor at a slow rate naturally, the speed is increased so that the phosgene is destroyed as fast as it enters. The harmless substances carbon dioxide and hydrogen chloride are formed, and these are completely adsorbed by a layer of special soda-



Permanganate or some other oxidizer is also present in the canister. It is packed with cotton wool or paper pulp for filtering out dusts.

PROCESSES OF MANUFACTURE

Phosgene is made by the catalytic combination of carbon monoxide, CO , and chlorine. The catalyst consists of carbon granules, and acts in two stages. A first iron box, 8 feet long, 2 feet 9 inches deep, and 11 inches wide, is immersed in cold water; in this box the conversion takes place to the extent of 50 per cent. A second box, to which the gas from the first box passes, is surrounded by hot water, and here the conversion is completed. The reaction is: $\text{CO} + \text{Cl}_2 = \text{COCl}_2$, phosgene. The finished material in gas form is purified by means of sulfuric acid towers, and is liquefied by passing it through lead coils laid in brine.⁴ The liquid phosgene is run into iron cans previously evacuated and cooled. From these it may later be run into shells cooled to -20°C .; the filling stations for this purpose are situated under hoods with fans, so that the escaping gas is drawn away and discharged into the atmosphere, or destroyed in scrubbing towers.

Phosgene is also a commercial chemical; it is used in organic reactions. Mustard gas, dichlorodiethylsulfide, $\text{CH}_2\text{Cl} \cdot \text{CH}_2 \cdot \text{S} \cdot \text{CH}_2 \cdot \text{CH}_2\text{Cl}$, is made by passing ethylene, C_2H_4 , into sulfur monochloride, S_2Cl_2 :



Free sulfur is formed at the same time free sulfur, as indicated in the equation. The removal of this sulfur caused much difficulty until it was found that by running the reaction at 30°C ., most of the sulfur remained in solution, and need not be separated at all. The product containing dissolved sulfur is nearly, if not quite, as active as pure mustard gas.

See "The manufacture, their action and control," by Joe L. Risinger, *Refiner and Natural Gasoline Manufacturer*, 21, 95 (1942).

When using a slight excess of carbon monoxide, practically all the chlorine is made to react; the carbon monoxide does not liquefy and is vented at the discharge point.

Ethylene for such emergencies is prepared by passing alcohol in vapor form over kaolin heated to 500° or 600° C.: $\text{C}_2\text{H}_5\text{OH} = \text{C}_2\text{H}_4 + \text{H}_2\text{O}$

Sulfur chloride is made in cylindrical steel tanks laid on their side. A batch of sulfur is placed in the tank, melted by the application of outside heat, and dry chlorine passed in. As the reaction proceeds, $\text{S} + \text{Cl}_2 = \text{S}_2\text{Cl}_2$, heat is evolved, and the tank must be cooled by a spray of water. After all the sulfur is converted, the sulfur chloride, a liquid with a characteristic odor, is run off and another batch started.

The sulfur chloride and ethylene are combined in the presence of mustard gas from a previous batch, which acts as a solvent, in the Levinstein reaction (English). The product is run to settling tanks, where a small amount of sulfur and sludge settles out; the supernatant liquid is pale yellow, and is ready for shell filling without further treatment. Pure mustard gas is a colorless liquid which melts at 13° C.; the product made as described contains impurities which lower the melting point.

Chloropicrin. In order to manufacture chloropicrin, $\text{CCl}_3 \cdot \text{NO}_2$, steam is passed through a mixture of calcium picrate and bleaching powder. The calcium picrate is made by neutralizing picric acid (Chapter 33) with lime.

Bromobenzyl-cyanide. The most effective lachrymator is probably bromobenzyl-cyanide, $\text{C}_6\text{H}_5 \cdot \text{CHBr} \cdot \text{CN}$, a liquid at summer temperatures.

The manufacture consists of the following steps: Benzyl chloride, $\text{C}_6\text{H}_5 \cdot \text{CH}_2 \cdot \text{Cl}$, made by chlorinating toluene at 100° C., is mixed with an equal volume of 50 per cent alcohol, and treated with sodium cyanide. Sodium chloride and benzyl cyanide, $\text{C}_6\text{H}_5 \cdot \text{CH}_2 \cdot \text{CN}$, form. The cyanide is subjected to fractional distillation and the fraction boiling within a few degrees of the boiling point (231.7° C.) is treated with bromine vapor mixed with air; the reaction is catalyzed by a small amount of bromobenzyl cyanide from a previous batch. The product obtained is freed by a stream of air from the hydrogen bromide formed at the same time, and is then sufficiently pure for use as a lachrymator. It has a low vapor pressure and thus is highly persistent.

Chloroacetophenone, $\text{C}_6\text{H}_5 \cdot \text{CO} \cdot \text{CH}_2\text{Cl}$, a solid, as effective a tear gas as bromobenzyl-cyanide, is produced from acetic acid, chlorine, and benzene. Acetic acid is chlorinated to form monochloroacetic acid, $\text{CH}_2\text{Cl} \cdot \text{COOH}$; this compound is then treated with chlorine and sulfur monochloride to form chloroacetylchloride, $\text{CH}_2\text{Cl} \cdot \text{CO} \cdot \text{Cl}$. The final step is the treatment of chloroacetylchloride with benzene in the presence of aluminum chloride to form chloroacetophenone.

*Lewisite*⁵ is a vesicant similar to mustard gas. The process for its manufacture was not developed in time for use during World War I. Acetylene is bubbled through a mixture of anhydrous arsenic trichloride and aluminum chloride; adsorption is rapid and much heat is developed. The reaction produces a heavy liquid consisting of three main fractions: the lowest-boiling one is Lewisite, a faintly yellow liquid, with composition $\text{CHCl} : \text{Cl} : \text{AsCl}_2$, chlorovinyl-dichloroarsine.

⁵ Green and Price, *J. Chem. Soc.*, **119**, 448 (1921). Lewisite is named after Professor W. Lewis of Northwestern University.

phenylchloroarsine, the sneeze gas applied in the form of atomized is made from diazotized aniline and sodium arsenite; numerous reactions are involved.⁶

CHEMICAL ADSORBENTS

The chemical adsorbents employed in the gas-mask canister for eliminating casualty-producing agents were soda-lime and charcoal; special procedures for their production were developed during the war. For the production of suitable soda-lime, the method consists of making a plastic mass of cement, kieselguhr, caustic soda, and water, spreading it in slabs on bottomed trays, allowing it to set two or three days under carefully-controlled conditions, drying, grinding, and screening to 8- to 14-inch mesh, finally spraying with a solution of sodium permanganate with a specially designed spray nozzle. A representative composition of such soda-lime would be:

	Per cent
Hydrated lime, $\text{Ca}(\text{OH})_2$	55
Portland cement	17
Kieselguhr	7.2
Sodium hydroxide, NaOH	1.2
Sodium permanganate, NaMnO_4	3.8
Moisture	15.7

Lime is the essential constituent for adsorption. The cement renders granules hard so that they do not form dust while the canister is in use; such dust would soon clog the canister. The loss in adsorptive capacity due to the presence of the cement is in part counterbalanced by the function of the bulky kieselguhr. Sodium hydroxide increases the capacity of the granules, and serves also to maintain the proper moisture content. This moisture content is very important in securing maximum gas absorption. The function of the permanganate is to oxidize arsine and other compounds.

The charcoal⁷ was made by carbonizing coconut shells, and for lack of coconut shells, by carbonizing fruit pits, walnut shells, hard wood, peat, and even anthracite. The charcoal found most efficient in adsorption was coconut charcoal, the efficiency of the others varying in the order mentioned; but all charcoals become useful, rapid adsorbers only after activation with steam, or steam and air treatment. The preparation of an activated charcoal, then, involves two steps: The formation of a porous, amorphous carbon at a relatively low temperature, followed by the removal of adsorbed hydrocarbons from the primary carbon, thereby increasing its capacity. The first step presents no serious difficulties since it simply involves a distillation at relatively low temperature. The second step is a more difficult matter. The procedure which has yielded best results to remove the adsorbed hydrocarbons by combined oxidation and distillation involving steam alone, or steam and air; the hydrocarbons of high boiling points are broken down into more volatile substances easily removed at lower temperatures and under conditions less likely to result in the deposi-

⁶ "Chemical warfare," Fries and West, New York, McGraw-Hill Book Co., 1921, p. 183, and *Ind. Eng. Chem.*, **11**, 825 (1919).
⁷ *Ind. Eng. Chem.*, **11**, 95 (1919).

tion of the secondary carbon, which is inactive. During the removal of the hydrocarbons by oxidation and distillation of the hydrocarbons, a loss in primary carbon by oxidation occurs; the condition of activation must therefore be so chosen that the hydrocarbons are oxidized rapidly, the primary carbon slowly.

In the steam-activation process, the charcoal is placed in an upright steel tube with top feed and bottom discharge; the tube is surrounded by fire gases which maintain its temperature at 800° to 1000° C. Superheated steam enters through an inner tube and streams downward through the charcoal, carrying away the undesired hydrocarbons before they can be decomposed by the high temperature and deposit inactive carbon. A certain amount of oxidation also takes place, for after the original carbonization, the charcoal is exposed to air which is adsorbed and thus carried into the activating chamber.

In the steam and air treatment, the temperature is 350° to 450° C.; the product is about the same as for the steam activation; each method has certain advantages.

Before activating, the charcoal is ground and sieved to the same size as the soda-lime granules.

The activity or adsorptive power of the charcoal is determined by passing a standard concentration of some gas, such as chloropierin, mixed with air, through a tube containing a standard amount of charcoal; the period of time which elapses before the chloropierin appears in the exit gases is a measure of the adsorptive power. An unactivated charcoal adsorbs the chloropierin from a 1 per cent mixture for about 2 minutes only, while activated coconut charcoal adsorbs for 58 minutes. The coconut charcoal produced during the war on the large scale was good for about 34 minutes under this test. The concentration of the test gas is much higher than that of the gases normally encountered in the field in warfare, so that the service of the gas mask canister is very much longer (say 100 times) than would appear from this test. Besides the soda-lime and charcoal adsorbents, the canister⁸ contains cotton pads for retaining dusts.

BY-PRODUCTS OF CHEMICAL WARFARE

Chemical warfare research and development have also resulted in many discoveries which are of vital importance in connection with the peaceful pursuits of the country. These by-products of chemical warfare include the use of chlorine as a cure for colds; the use of chloropierin as an insecticide for treating stored grain; the use of cyanogen chloride with hydrocyanic acid for the fumigation of ships and warehouses, valuable because cyanogen chloride is a tear gas as well as a fumigant and serves as warning that dangerous concentrations of hydrocyanic acid gas are present; the use of tear gas for the control of mobs, and the subjection of criminals; and the adaptation of the army gas mask for the protection of those who manufacture or use industrial poisonous gases and dusts. Industrial gas masks are similar to the army gas mask except that special canister adsorbents are

⁸ A canister with one side replaced by glass so that the contents are visible may be purchased for a small sum from the Mines Safety Appliances Company, Pittsburgh, Pa., and is well suited for exhibition in the class-room or museum.

ed to afford protection against the particular industrial poison or noxious which may be encountered; there is also an all-purpose canister which affords protection against all poisonous gases and smokes which might be inhaled by firemen in fighting fires. (Compare also p. 639.)

Chemical warfare research is therefore of importance not only to provide national defense in the event of war involving the use of chemical agents, but also to provide knowledge concerning the effective use of industrial poisons, and to furnish methods of protection for those who may encounter poisons in their work.

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In scientific laboratories, the researcher quite naturally seeks to obtain crystallizable solids, rather than non-crystallizable ones, generally dubbing "tars." By means of crystallization, he can purify his new substance; pure substances alone can the constitution of its molecules be settled beyond doubt. The synthetic resins have afforded the first big lesson to the chemical investigator, that the humble "tars" may have their uses. Other methods of purification besides crystallization have been developed, and entire new techniques permit the study of the polymerization or condensation product. With other chemical discoveries, that of the synthetic resins being no means less important, and still means, increased capacity for service to man on the part of science, mainly in new directions.

Chapter 35

Synthetic Plastics, Synthetic Resins

Synthetic plastics¹ have found numerous uses, and have met many new and difficult requirements. They are light, durable, readily molded to intricate shapes; most of them are unaffected by moisture, so that they do not warp. The clear, transparent plastics are supplemented by others which are colored every conceivable shade, so that plastics have beauty appeal. Finally, the synthetic plastics are comparatively inexpensive.

The synthetic plastics are generally grouped into two classes depending upon their behavior on heating. A substance may be thermoplastic or thermosetting. A thermoplastic substance such as Vinylite, cellulose ester, methyl methacrylate, and polystyrene, softens on heating to a plastic mass which may be shaped, and which hardens on cooling. It will soften once more when heated a second time, and harden on cooling as before. The process may be repeated any number of times. The thermosetting resins, such as the standard phenol-formaldehyde or urea-formaldehyde resins, hardens on heating to an infusible mass; the set is permanent.

A very useful classification is one based on chemical composition, which has three main classes: (a) the cellulose derivatives, nitrated cellulose, pyroxylin, cellulose acetate, cellulose aceto-butyrate, ethyl cellulose; (b) the synthetic resin plastics, phenol-formaldehyde, urea-formaldehyde, and alkyl resins, the acrylate resins; (c) protein resins such as those derived from casein.

Synthetic resins may be so prepared that they are "oil-soluble," while they become the important film-forming material in protective coatings. Cellulose derivatives, especially cellulose nitrate, may function in a similar capacity.

CELLULOSE PLASTICS

The cellulose plastics are made from cotton linters generally.

Nitrated cellulose or pyroxylin contains 11 to 12 per cent nitrogen.

¹Plastics are bodies which under the influence of heat and pressure become soft enough to be pressed, formed or shaped, while after cooling they are rigid again; or bodies which soften under the influence of heat and may be molded under pressure when so heated, but which harden on cooling, and after cooling may no longer be softened by heat; or bodies which made up with plasticizers are soft and may be shaped, retaining the shape permanently after the removal of the plasticizing agent. The clays belong to the third class.

gun cotton contains a more highly nitrated cellulose, with 12.5 per cent nitrogen. The preparation of pyroxylin has already been given, in Chapter 31. In order to prepare the plastic, the nitrated cellulose is dissolved with camphor and alcohol, filtered, and the filtered solids mixed with plasticizers (other than camphor), dyes and pigments, and block oil added to give flexible pyroxylin sheets.

A well-known pyroxylin plastic is Celluloid,² a solid which softens at 100°C., at which temperature it may be pressed, twisted and shaped in various ways to forms which after cooling are persistent. It consists of nitrocellulose (2 parts) and camphor (1 part), with one or several other substances added to stabilize it and give it color. An early formula was:

	Parts by wt
Camphor or camphor oil	20
Castor or linseed oil	40
Nitrocellulose or "xyloidine"	40

The method of preparation consists of mixing the water-wet nitrocellulose with powdered camphor, sprinkling alcohol on the mix, and kneading at low temperature for several hours. At this lower temperature (35°C.) the operation is safer than at the higher temperature necessary for drier materials. The resulting mass is soft, and by heat and pressure it is formed into sheets, blocks, and other shapes.

Pigments are incorporated during the kneading; zinc white for example gives a white resembling ivory. For transparent plastics, urea is added as a stabilizer (antacid); in the white Celluloid, the zinc oxide is both pigment and stabilizer.

There is another method practiced chiefly in Europe, in which an alcohol solution of camphor is allowed to stand over pyroxylin, and after some time all are mixed under heated rolls; the solvents are recovered. The soft mass is shaped as stated above.

Camphor not only plasticizes pyroxylin, but robs it of its explosive character; the plastic remains flammable, however, but hardly more so than other combustible material. The shaped articles must be allowed to stand in closets at 30°C., until all solvents have evaporated.

A special kind of pyroxylin plastic is used for the manufacture of moving-picture films; the camphor for this purpose is usually purified by solution in alcohol and filtration; the formula specifies a higher proportion of pyroxylin which is dissolved in methanol, amyl acetate, and other combinations of solvents, to produce at once a thick solution low in camphor (3 per cent). This solution is fed to a large cast-iron wheel (15 feet in diameter or larger), perfectly balanced, with its 18-inch face silvered and polished: the wheel turns slowly, so that the liquid fed in at one place dries sufficiently for nit removal before a whole revolution has been made. The film is continuous, and wide enough to give a number of strips of the standard width (2 mm. wide) for moving-picture cameras. The film base, after suitably drying, is coated with the gelatin carrying the silver salts.³

² The name was coined by the Hyatt Brothers; John Wesley Hyatt took out many patents, for U. S. Patent 88,633 in 1869. In that day, the development of the new plastic was a greater achievement than that of the synthetic resins has been in the past decade. Other similar plastics are Celluloid, Fiberloid. The word nitrocellulose is still in general use and means nitrated cellulose.

There are a number of other formulas for pyroxylin plastic films moving pictures. In addition cellulose acetate film, which is not flammable, has been introduced. Following fatal explosions traced to stored X films of pyroxylin, tests were made⁴ with cellulose acetate films, and showed them to be essentially unaffected by the temperatures and long heating which produced explosions and toxic gases with the pyroxylin film.

In order to reduce the flammability of pyroxylin plastics, denitration, not proved satisfactory, as it interferes with the plasticity of the material. Salts such as magnesium chloride have been added, with more success.

Fabrikoid is a material which resembles leather and serves many purposes. It is made by coating cloth with pyroxylin made into a free-flowing jelly by the addition of suitable solvents.

Camphor. Natural camphor is obtained from the camphor tree, *Laurel camphora*, which grows in Japan and in Formosa. The tree, prefered 50 years old, is chopped small, and boiled with water at a slow rate; escaping steam carries the camphor away to the condenser, where the camphor forms a crust on the condensed water. The crude material obtained is pressed free of the greater part of the camphor oils, and purified finally by sublimation.

Synthetic camphor, $C_{10}H_{16}O$, a white solid, is manufactured in the United States, at the rate of 4.5 million pounds a year (1941). The material is pinene, itself obtained from turpentine.

Instead of camphor, other substances have been successfully used as plasticizers for pyroxylin, particularly tricresyl phosphate, a liquid, and triphenyl phosphate, somewhat dearer, a solid. They are made by heating cresol or phenol with phosphorus trichloride in the presence of aluminum chloride.

For the preparation of *cellulose acetate*, the cotton linters are treated with acetic acid and acetic anhydride in the presence of a catalyst such as sulfuric acid in the acetylator, a vessel which may be tipped, and which is provided with an agitator. The acetylated cotton suspension is poured into a washer, where all the acid is removed, and later recovered. The cellulose acetate is kneaded with plasticizers and solvents, filtered, mixed with other plasticizers, dyes and pigments as required, and pressed into blocks, sheets, or extruded as rods and tubes. The method for the preparation of the cellulose aceto-butyrate is the same except that butyric acid as well as acetic acid acts on the cotton. The plasticized aceto-butyrate has lower moisture absorption and better weathering resistance than the straight acetate. Both acetate and aceto-butyrate may be ground into molding powder.

Photographic films and moving picture films may be obtained on cellulose acetate plastic, as well as on the cellulose nitrate plastic. The acetate film is a safety film.

There were produced in 1939 13,357,116 pounds of pyroxylin sheets, rods and tubes; of cellulose acetate 8,743,139 pounds; of molding composition

⁴ "Jahresbericht VII der Chemisch-Technischen Reichsanstalt," Berlin, Verlag Chemie, 1928, pp. 110-111.

7.032 pounds. The prices were, respectively, 76 cents, 75.5 cents, and cents a pound.

alkali cellulose and ethyl chloride heated in a pressure autoclave react to form ethyl cellulose, which is later mixed with plasticizers and pigments to make molding and extrusion compound.

SYNTHETIC RESIN PLASTICS

The synthetic resin plastics as already said comprise the phenol-formaldehyde resins, the amino resins, such as urea-formaldehyde resins, the alkyd resins, the methyl methacrylate resins, polystyrene, polyvinyl acetate and others.

The manufacture of resins requires simple apparatus; the process consists a rule in mixing two liquids, or a solid and a liquid, heating them to produce the reaction, removing any water formed, then heating the product further with, or without, additions, until a test sample shows proper melting point and viscosity. The end point is not definite, and a variety of intermediate products may be obtained. Uniform products are obtained only by taking the same quantities, heating to the same temperature for the same length of time, with all other conditions identical. Not only the length of cook, and temperature, but the absence, presence, and amount of catalyst influence the properties of the product.

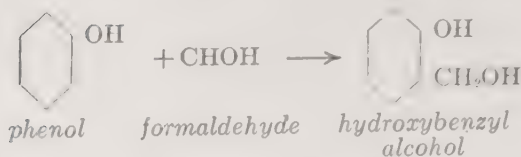
The depth of color of the product depends partly on the degree of purity of the raw materials; in general, the darker these are, the darker will be the product.

In order to produce synthetic resins at reasonable prices, inexpensive raw materials must be available. The chief raw materials are urea, formaldehyde, phenol, phthalic anhydride, acetone, methanol, acetylene and glycerol. Stimulated by the possibility for considerable consumption in the resin manufacture, the production or recovery of these materials has progressed rapidly to insure abundant supplies at relatively low prices. The resins using phenol, whether recovered or synthetic, or phthalic anhydride, or phthalic anhydride, may be considered as of coal-tar origin. The non-coal-tar resins are designated in the more detailed presentation which follows. Synthetic resins may be the products of condensations, that is, reactions which involve the formation and elimination of water or other simple substance and the union of the large remainders; or they may be the product of polymerization. In general, the products of condensation are thermosetting resins, the products of polymerization thermoplastic resins.

Phenol or cresol-formaldehyde condensation products. This development proceeded along three different lines, all leading to a final infusible product: (1) Methods employing ammonia or a metallic base such as caustic soda as the catalyst;⁵ (2) Methods using no condensing agent, but an elevated temperature, or else an acid catalyst, with the subsequent addition of methylenetetramine;⁶ and others, in which phenol, hexamethylene-

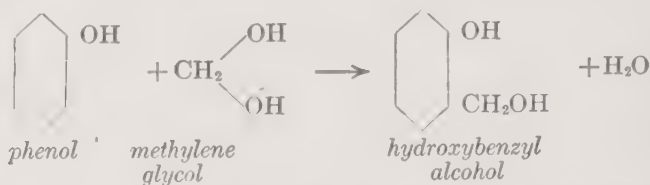
⁵ Patent 942,809 (1909); the previous patent to Baekeland does not mention the catalysts,

⁶ Patent 1,020,593, the Aylsworth patent.



tetramine, and anisole are used, permitting an anhydrous reaction;⁷ in a later patent, the anisole is omitted.⁸ (3) Methods in which hydroxybenzyl alcohols are consciously formed and condensed further with the addition of a base as condensing agent.⁹

By writing formaldehyde in its hydrated and no doubt true form when in solution, as methylene glycol, the reaction is clearly shown to be a condensation reaction, and it becomes more understandable: $\text{CHOH} + \text{H}_2\text{O} = \text{CH}_2(\text{OH})_2$, and



Procedure. In a general way, the procedure in these three methods is the same. The phenol in liquid form,¹⁰ and the formaldehyde as 40 per cent solution, equal parts by weight, are placed together in a kettle fitted with a reflux condenser; the two liquids are miscible. 0.5 to 5 per cent catalyst (on the weight of the phenol) is added, selected from a long list of materials, basic or acid, organic or inorganic. Gentle heat is applied so that the liquid boils quietly. After 2 hours or so, the upper water layer which gradually separates has reached a maximum, and is run off. The lower thin-flowing liquid (while warm) is resin A, which on cooling hardens to a brittle solid, soluble in organic solvents.

The proportion of the reactants, and of the catalyst, may be varied; the catalyst may be acid or basic.

For casting-resinoids the "one-step" process is usually used. In this process the reactants are employed in theoretical proportions. They are heated in the presence of the catalyst until the resinoid separates. The supernatant water is removed, the resin dehydrated, and poured into mold. It is then polymerized under heat and pressure until it is infusible. The infusible cast shapes are sold to the trade to be cut, sawed, sanded, drilled or turned, as desired, using equipment similar to that used in wood working. Pipe bits, beads, cutlery handles, and the like are thus made.

Resinoids suitable for molding are usually made by the two-step process. In this process the phenol is employed in excess. The reaction is similar to the one-step process. The fusible dehydrated resin is run into pan, cooled, then an intimate mixture of this fusible resin, with hexamethylene tetramine sufficient to render the fusible resinoid infusible when heated.

⁷ U. S. Patent 1,209,333 (Redmanol).

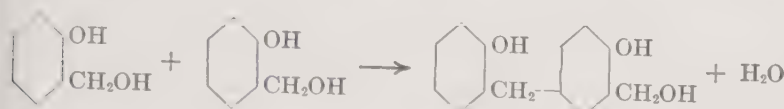
⁸ U. S. Patent 1,230,829 and U. S. Patent 1,310,088 (Redmanol).

⁹ Brit. Patent 15,517 (1905), the de Laire patent.

¹⁰ Phenol is solid melting at 40.8° C.; 2 per cent water liquefies it.

a filler, usually wood flour, are ground together in a ball mill. The fine mixture constitutes the molding powder sold commercially. Such a mixture is charged into a steel mold and subjected to heat and pressure to produce an infusible, rigid molded article. Closures, electrical equipment, telephone parts, automotive parts, and the like are thus manufactured. The dehydrated, unpolymerized resinoid, as obtained from the one-step process, is dissolved in a solvent, it constitutes the varnish used for impregnation of paper, fabric, or the like. If such impregnated paper or fabric is piled sheet on sheet to the thickness desired and the whole subjected to heat and pressure, there are produced so-called laminated plates, known as panels, laminated gears, etc.

At a very early date, the patent of the French firm de Laire¹⁰ had indicated that the resins obtained by heating phenol alcohols were the result of the condensation of several of these. The starting materials were phenol and hydrated formaldehyde, and the process of phenol-alcohol formation took place first, with the further condensation to an intermediate or final product as follows:



For the preparation of the phenol alcohols is made.

The formation of phenol alcohols was not recognized by the early scientists. Investigators of the phenol-formaldehyde reaction, because an acid catalyst was employed, which favors the condensation of the phenol-alcohol, so that their presence escapes notice. With the introduction of alkaline catalysts, which catalyze only slowly the phenol-alcohol condensation, the existence of such alcohols was established.

A few words must be said regarding the preparation for molding compounds. For these, "an intimate mixture is prepared from the fusible resin, wood flour, and the desired coloring matter, if any, by grinding them together in a ball mill, hot-rolling the mass, again grinding, and screening, to insure absence of foreign matter." To lesser extent, other fillers are used. "At the temperature given by 125 to 175 pound steam, such a molding compound quickly fluxes, and then as quickly solidifies in the heat that first produces it."¹¹

Processes have been developed which allow the production of any desired color (see Spirit-soluble dyes, Chapter 28). The filler will in many cases influence, or influence, the color; fillers are: wood flour, zinc oxide, barium carbonate, calcium sulfate, graphite, pumice, lampblack, ground asbestos, mica, and many others.

Time required for heat-hardening. In the case of the Bakelite molding compounds, the time required for molding depends upon (a) the particular composition of the molding compound, (b) the thickness of the piece, (c) the temperature of curing, (d) the type of mold. In average molding practice, with the mold at a temperature of 350° F. (177° C.), thin articles

¹⁰ V. H. Mory, "Nature was suitably aided," *J. Chem. Ed.*, **6**, 617 (1929).

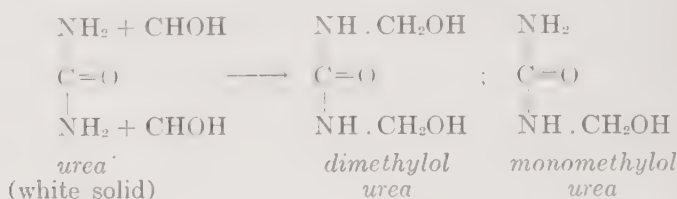
such as buttons can be molded in about 45 seconds and discharged without any cooling. Thick pieces, such as 1 inch in thickness, require 10 to 30 minutes and are cooled some time in the mold, especially if the dimensions have to be held accurately. For the average run of pieces, such as automatic distributor heads, radio tube bases, and similar ones, the time is run between 1 and 3 minutes.

Phenol may be condensed to a resin with the aid of furfural, producing interesting products with merits of their own (Durite). There are furthermore furfural resins in which no phenol is used which are giving good results.

(b) **Urea-formaldehyde condensation products representing the amino plastics.** The urea-formaldehyde condensate is one of the products which in their final state are as clear, transparent, and colorless as glass. Other plastics are the alkyd resins, vinyl resins, methyl methacrylate resins, and styrene resins. The urea-formaldehyde condensate is essentially unbreakable.

One mol of urea and 3 mols of formaldehyde are heated in the presence of hexamethylenetetramine;¹² the initial condensation product is a liquid, soluble in water; on heating further, an intermediate rubber-like product is formed, insoluble in water. Continued heating, or combined heat and pressure, yield a hard, infusible, transparent mass, insoluble in acid or alkali.

Urea and formaldehyde form mono- and dimethylol urea; it is the monomethylol urea which is probably the chief constituent of the resin. Dimethylol urea, heated alone, changes at 126° C. (258° F.) to a liquid, then at 137° C. (278° F.) to an amorphous white body which does not melt on further heating but decomposes at 260° C. (500° F.).



The first, highly viscous product may be mixed with a filler and coloring matter, and then hardened. Below 50° C. (122° F.) it does not change, but above it, the desired hardening takes place.

On adding carbamide, there is formed the white condensation product of this substitute with excess formaldehyde, and the resulting resin on being hardened yields masses similar to white milk glass.

"Plaskon" is a urea-formaldehyde molding compound, made with special care as to combining proportions, removal of unreacted components and several other cautions, so that it is successfully used as a material now standard for the manufacture of scales. Plaskon is produced as granules or as powder, and is used clear, or with fillers. When first heated in the mold it becomes plastic, then sets strong and rigid. The molds are heated with 100-lb. steam for thin walls, by 60-lb. steam for $\frac{1}{4}$ -inch walls and over.

The urea-formaldehyde resins were slow molding; this character-

¹² Brit. Patent 171,094 (Fritz Pollak).

¹³ "Systematic study develops new molding compound," A. M. Howald, *Chem. Met. Eng.*, 35 (1931).

been improved considerably, so that now their molding time is equivalent to that of the phenol-formaldehyde powders. The main outlet for urea-formaldehyde molding powders has been for articles, parts for scales, drinking tumblers, and similar pieces.



FIGURE 196.—The Plaskon Duplex Scale, to show the one-piece housing of Plaskon, a urea-formaldehyde plastic. (Courtesy Toledo Scale Company.) Width, 17 $\frac{3}{4}$ " ; depth, 15 $\frac{3}{4}$ " ; height, 15 $\frac{3}{8}$ ".

Phenol-furfural. Furfural (300 pounds) and urea (100 pounds) heated in the presence of a catalytic agent (4 pounds 26 per cent aqua ammonia), and a hardening agent, give a product which is convertible by heat into an insoluble body.¹⁴ With 5 per cent Chinawood oil, the final material is more durable.

Urea-formaldehyde resins are not manufactured in the United States, but are made in England.¹⁵

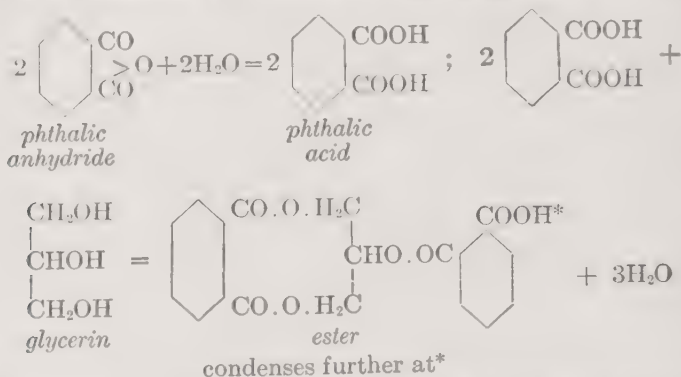
Many proposals for the production of phenol-furfural condensation products have been made (see item "Other Patents" at the end of the chapter) but have not become very important commercially.

Phthalic anhydride-glycerin condensation products representing thermosetting resins. When 2 parts of phthalic anhydride (a white solid) and 1 part of glycerin are heated slowly at 100° C. (212° F.), there results a thick liquid. On continuing the heating to 185° C. (365° F.), there is some thickening; when this is over, the temperature is raised to 210° C. (410° F.).

U. S. Patent 1,827,824.
Am. Met. Eng., 40, 42 (1933).

The first stage of the reaction is now complete. The product when cooled is a yellowish, transparent solid, soluble in acetone. The resin may also be water-white or transparent.

Heated several hours to the moderate temperature of 85° to 105° (185° to 221° F.), after the incorporation of filler, pigment or dye, or without these, the material is hardened to the hard infusible resin, without bubble formation.¹⁶ A high luster is given by the contact with the mold. The type of condensation is pictured in the equations below:



This is not the exact molecular size of the resin, which is more likely to be of the order of 5000.¹⁷

The advantages which the molded and heat-hardened resin articles offer are: resistance to water and most chemicals, and to mechanical shocks, high dielectric value, low density, structural strength, and low heat conductivity. The plastic property of the initial material allows versatility of form. The hardened resins and the molded products may be cut, threaded, and machined.

The major use of molded products of heat-hardened resin plastics is in the manufacture of electrical insulators for the automobile radio, telephone and airplane trade. The resins are used in increasing quantities for ornamental fittings, dials, noiseless timing gears, smokers' articles, bottle tops (drugs), clock cases, door handles, and numerous other purposes. Molded resins have become of value in chemical engineering; tanks as large as 9 feet in diameter and 10 feet high, with no reinforcement aside from an asbestos filler, have been constructed. Another example is spinning buckets for viscose rayon. As molded resin does not warp, it is valuable as a frame for delicately adjusted electrical instruments, as well as for their cases.

A new and promising plastic of the phenol-formaldehyde type has for some time been on the market under the trade name of Haver. As it is particularly adapted to the fabrication of chemical equipment it will be described in Chapter 45.

Laminated products consist of sheets of suitable material, such as paper, fiberboard, fabrics, coated on both sides with a solution (acetone, alcohol,

¹⁶ U. S. Patent 1,108,329.

¹⁷ For a hard transparent resin from ethylene phthalate, 25 structural units are assumed and a molecular weight of 4000; for a soft, transparent resin from tri-methylene phthalate, 14 structural units are accepted, molecular weight of 1700. The condensed ester as written above would probably be the same one structural unit. Compare W. H. Carothers, "Polymerization," *Chem. Reviews*, 8, 365 (1934).

TABLE 85.

Resin	Tensile Strength lbs. per sq. in.
Pure phenol-formaldehyde after hardening by heat	5,000-11,000
Pure phenol-formaldehyde with a filler	6,000-12,000
Urea-formaldehyde	5,000- 6,400

uncured resin. The material is pressed, dried and then hot-pressed at the resin sets.

Motor windings and coils for auxiliary devices may be "set" in resins. Particularly phenol-formaldehyde resin, itself a good insulator, by placing the coils in an autoclave filled with the fused uncured resin. After immersion, the excess resin is run off, the vessel closed tight again, and the subject is subjected to the heat-hardening process under pressure.

1) **Acrylate resins.** The methyl methacrylate resin plastics enjoy a special and well deserved distinction at the present time, because they are sold under the name of Plexiglass, for making the curved hood protecting the cockpit in many types of airplanes.^{17a} Plexiglass is transparent, colorless, clear as glass; it is essentially unbreakable, strong, and difficult to burn on fire.

Methyl methacrylate $\text{CH}_2 : \text{C}(\text{CH}_3) \cdot \text{COOCH}_3$, a liquid, is polymerized with heat, light, benzoyl peroxide, sodium peroxide, giving products which range from soft solids to hard solids, depending upon the degree of polymerization. Plexiglass is the hard substance, polymethyl methacrylate. Lucite is made into curved rods which carry the light into the cavities of the body for the greater convenience of surgeons. The polymethyl methacrylate resins are thermoplastics.

TABLE 86.—*Synthetic resins: United States production and sales in 1940.**

Coal-tar resins		
	Pounds	Value per pound
Alkyd resins:		
Maleic anhydride resin	6,476,883	\$0.19
Phthalic anhydride resin	91,446,195	.18
Coumarone and indene resins	24,131,733	.07
Polystyrene	n. r.
Cresylic acid resin	11,978,763
Phenol-formaldehyde resins:		
For casting	6,953,103	.47
For molding	26,417,693	.31
For other uses	26,957,636	.20
Phenols and cresol resins	21,126,005
Total coal-tar resins	222,943,118	.22
Non-coal-tar resins		
Urea-formaldehyde resins	21,491,653	.39
Other non-coal-tar resins are the resins made with Abietic acid, Acrylic acid esters, Melamac, Petroleum, Polyamide, Polyvinyl alcohol, Sebacic acid, Terpenes, Urea and thiourea, Vinyl acetal and vinyl butyral, Vinyl acetate and chloride, and Vinylidene chloride polymer.....		
Total non-coal-tar resins	53,871,245	.55

* Trade Commission Report No. 148 (part.—no record).

^{17a} Working transparent plastics," by John Sasse, Aviation Magazine, May 1942, pages 86-95.

Other polymerized resins are Vinylite, polymerized vinyl chloride, which in blocks of some thickness is water white and transparent to ultraviolet light; polystyrene, from styrene $C_6H_5 \cdot CH : CH_2$, a liquid; Cumar, a polycoumarone-indene resin, made from coal-tar naphtha. There are many other resins and resin plastics, and new ones in process of development. The properties of the final material may be modified to meet requirements by polymerizing two different molecules, and furthermore by varying their respective proportions.¹⁸ Polymerization is possible whenever there is a saturation in the molecule.

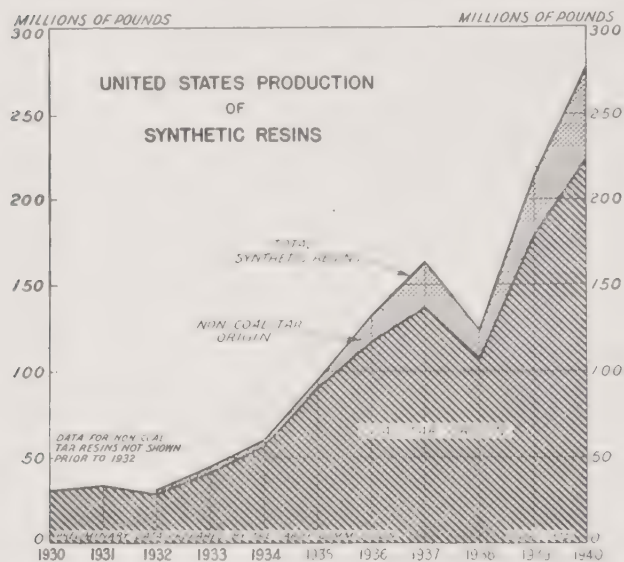


FIGURE 197.—The production of synthetic resins over a period of years in the United States. (From Industrial Reference Service, U. S. Department of Commerce under title "Plastics: The Miracle Material," by J. I. Taylor, September, 1941.)

The thermoplastic molding powders are well handled in injection molding machines, while the thermosetting resin plastics continue to be handled in the older compression molding presses. These latter have a mold which is cored for the circulation of steam for heating and cold water for chilling; the cycle is necessarily longer, since a reheating of the mold follows each cooling. In injection molding, the thermoplastic powder is heated outside the mold, in a cylinder where it is compacted, and from which it is extruded into the cold mold. Here it chills and solidifies enough to permit automatic ejection. The injection molding machines are high-speed automatic machines. Extrusion molding is an extension of injection molding.

OIL-SOLUBLE SYNTHETIC RESINS

The oil-soluble resins are materials differing markedly from those discussed in the previous paragraphs, for one of the properties of molding resins is oil-insolubility. This class on the contrary must possess solution properties when added to Chinawood oil, for example, in order to be used.

¹⁸ Ideal conditions for polymerization are: (1) the double bond; (2) the conjugated double bond; (3) unsymmetrical arrangement; (4) formation of mixtures; (5) position isomers; (6) variable chain lengths; (7) multiple functional groups; (8) formation of long chains; (9) associate linkage; (10) substituting hydrogen by negative groups enhances the polymerizing power; but only up to a point; too much negativity inhibits polymerization. Finally, in general, the more highly polymerized the molecule, the harder the resin.

in-forming constituents in varnishes. Some of the oil-soluble resins are for molding, modified by a subsequent treatment which introduces a drying agent; others owe their properties to admixtures in the original formula for making the resin, and are therefore distinct products. The important representatives of this type of resins are given below. *Ester gum* is glyceryl abietate, also called glyceryl resinat, and is made by melting rosin with 11 to 12 per cent of its weight of glycerin, distilling off the water formed. The product after cooling looks very much like rosin, and has a faint odor similar to that of rosin, but it is less brittle, its acid number is 15 and less instead of 165; this means a greater solubility in water. It has all the remarkable oil-solubilities which rosin has. Rosin is essentially abietic acid, $C_{20}H_{30}O_2$, with which glycerin forms ester; glycerin triresinate is the preferred form,¹⁹ but the commercial product usually contains small amounts of di- and mono-resinates.

Rosin + glycerin = ester gum + water

Phenol-formaldehyde resins dispersed in ester gum are available under several trade-names.²⁰ Since 1928, there has been available a 100 per cent oil-formaldehyde oil-soluble varnish resin.²¹

Glycerin and phthalic anhydride condensed in the presence of the fatty acids from linseed oil yield oil-soluble resins, such as "modified glyptal," which have proved very satisfactory. "Oil-soluble Rezyl" is another well-known representative of this class, and contains fatty acids, or rosin, or

"Oil-soluble Teglac" is a glycerin-phthalic anhydride condensate modified by rosin principally.

The oil-soluble alkyd resins²² are a group of resins including among them an ethylene glycol-phthalic anhydride condensate modified by unsaturated fatty acids from a drying oil. In general the oil-soluble alkyd resins for varnish making may be said to be esters of polybasic acids and polyhydric alcohols, modified by unsaturated fatty acids such as oleic acid, and the oils of the drying type.

In the process of development are resins produced from unsaturated petrochemical hydrocarbons (the di-enes), polymerized by the action of aluminum alkyls. Such resins do not yellow, and are on the acid side; at present, alkali is generally incorporated. For a high yield of resin a highly unsaturated distillate rich in diolefins and olefins²³ is best suited; a number of reactions take place simultaneously. The one leading to resins is controlled in part by the amount of catalyst, namely 2 per cent, and is favored by the presence of the proper ratio of diolefins and olefins,²⁴ which undergo polymerization. Olefins alone lead rather to synthetic lubricating oils.²⁵ *Isocolors* are chlorinated biphenyls, sold in the form of thick oils or resinoids, whose chief use is in lacquers. The nitrocellulose film contain-

Art Varnish Prod. Mgr., 8, Dec., 1932, sect. 1, p. 5.

known as Amberol, Beckacite; but it should be remembered that the trade name does not establish the nature of a product; under the same name, several products may be made.

313. "Protective and decorative coatings," vol. I, Joseph Matello, New York, John Wiley & Sons, 1941.

Ind. Met. Eng., 39, 599 (1932).

A diolefin $CH_2=CH_2$ is the simplest olefin; a diolefin has two double bonds; there are cyclic olefins as well as non-cyclic ones.

J. Eng. Chem., 24, 1125 (1932).

J. Eng. Chem., 23, 604 (1931).

ing an aroclor is more nearly fireproof, and also more brilliant. The aroclors are not oil-soluble.

Halowax is a chlorinated naphthalene produced either in the form of wax or an oil. The wax is used as condenser impregnation; in moisture- and flame-, acid and insect-proofing wood and fabrics and in moisture- and flame-proofing wire and cable. The oil is a good solvent for rubber and can be mixed with asphalt, wax, pitch, etc. It is used as a lubricant, a plasticizer and as a standard for testing index of refraction.

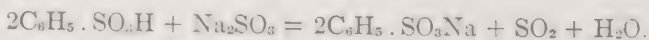
Mowilith, a recent addition to the long list of synthetic resins and resin-like products is produced in two steps. Monochloroacetic acid and acetylene react with mercuric sulfate as a catalyst, at 70° C. (158° F.), followed by further condensation under the influence of ultra-violet light. It is soluble in the lacquer solvents.

SYNTHETIC PHENOL

The rise in the production of phenol resins of various kinds made it imperative that new sources of phenol be found. Natural phenol is obtained from coal-tar. Synthetic phenol is made from benzene, by one of the following methods: sulfonation followed by alkaline fusion, or by chlorination and subsequent heating under pressure with caustic soda solution, or by the vapor phase regenerative process. The war emergency has made it necessary that military needs for phenol be filled first; it is indeed a fortunate circumstance that these several methods for obtaining phenol had been developed and well established.

There were produced in 1940 23,967,560 pounds of natural phenol, and 72,187,520 pounds of synthetic phenol. The natural phenol sold at 9 cents a pound.

Benzene Sulfonate Method. In the early developments, benzene chloride was treated with oleum,²⁶ the benzene sulfonate $C_6H_5 \cdot SO_3H$ was isolated by neutralizing both excess acid and sulfonate with lime, and filtering the calcium sulfate from the solution of calcium benzene sulfonate. An improvement was made when the continuous sulfonation method of Deming and Bull was installed.²⁷ Four sulfonating tanks are used in series, and in each, the benzene enters at the base through perforated pipes, so that it rises in the form of fine droplets. The sulfonated benzene remains dissolved in the great excess of benzene which is provided. The benzene flows counter-current to the acid; the latter is 98 per cent H_2SO_4 at the entry to the first tank, 77 per cent at the exit of the fourth, when its sulfonating power is exhausted. It is concentrated to 93 per cent and new oleum is added to it to reach the required 98 per cent strength. The benzene with 2 per cent sulfonate is washed with water (3 washers), the sulfonate in the water solution neutralized with sodium sulfite recovered from the last step in the process, and concentrated.



The strong solution of sodium benzene sulfonate is run, gradually, into fusion

²⁶ Chapter 27.

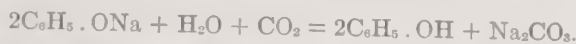
²⁷ *Ind. Eng. Chem.*, 10, 733 (1918).

soda at 320° to 350° C. (608° to 662° F.); sodium phenolate and sodium sulfite are formed.



The melt is dissolved in a limited amount of water, sufficient to dissolve sodium phenolate only; the sodium sulfite remains as a wet solid, which after washing and drying, serves for the neutralization of new amounts of the sulfonate. Only half the sulfite produced is needed in this way; the other half may be sold (by-product).

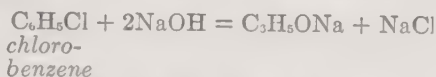
The sodium phenolate in solution is decomposed by carbon dioxide from the kiln; phenol and sodium carbonate are formed.



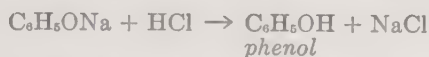
The latter is causticized by lime from the kiln. To complete the reaction, a small amount of nitre cake is added. The phenol separates as an upper layer; it is run off and distilled from a pot still.

Chlorobenzene Method. For many years attempts were made to produce phenol commercially from chlorobenzene, without result. It remained for an American firm to discover the proper apparatus, reaction mix and operating conditions which have made the process a commercial success. Starting with chlorobenzene, the method as practiced is as follows:^{28, 29}

Chlorobenzene (1 mol) is emulsified with a 10 per cent aqueous caustic solution (1½ mol) and the emulsion (oil droplets in water) pumped under a pressure of 200 atmospheres into a multitubular reaction vessel. Recirculation, and continuous discharge of a small portion which is just stirred up by the entering emulsion. The liquid travels through the tubes with sufficient turbulence to maintain the dispersion of the chlorobenzene. The tubes are made of copper, in several units 1½ inch outside diameter, with thick walls; a temperature of 320° C. (608° F.) is maintained by means of diphenyl oxide vapor under moderate pressure. The copper wall acts as catalyst. As the phenolate forms, it dissolves in the water. The conversion is nearly 100%, if the circulation period allows any one part of the liquid to remain within the tubular vessel for 50 minutes. The reaction is:



After leaving the reaction vessel, the liquid passes through the exchanger with the incoming liquids, then through coolers, after which the pressure is released. The free phenol is formed by a treatment with acid, giving phenol.



The upper layer is run off and distilled from a chromium-plated still,³⁰ and the water passes over first, next any unchanged chlorobenzene, near 132° C. (270° F.), then the phenol, near 181° C. (358° F.), while diphenyl oxide

J. Eng. Chem., 20, 114 (1928).

U. S. Patent 1,607,618.

U. S. Patent 1,824,867.

remains in the still. The latter's boiling point is 259°C. (498°F.). The recovery of phenol is nearly the theoretical one.

Raschig Method. The Raschig method for making phenol, also called the "vapor phase regenerative process," is producing at a rate exceeding a million pounds of phenol a year.³¹ The process is in two stages. In the first, monochlorobenzene is produced by the action of a catalyst from benzene, hydrochloric acid and air, in a first converter. $\text{C}_6\text{H}_6 + \text{HCl} + \frac{1}{2}\text{O}_2 = \text{C}_6\text{H}_5\text{Cl} + \text{H}_2\text{O}$. In a second converter, the chlorobenzene is hydrolyzed catalytically with steam, producing phenol and regenerating the hydrochloric acid for further use. $\text{C}_6\text{H}_5\text{Cl} + \text{H}_2\text{O} = \text{C}_6\text{H}_5\text{OH} + \text{HCl}$.

Still another method has been described briefly in a letter.³²

An attempt has been made to hydrolyze benzene sulfonic acid with aqueous caustic,³³ under pressure and at elevated temperature, as in the chlorobenzene method.

It has been proposed to make phenol from benzene by sulfur trioxide action in liquid sulfur dioxide.³⁴

Uses. The main consumption for phenol in peace time is the synthetic resin industry. A sizable quantity serves as disinfectant and preservative while about 4 million pounds a year are the starting material for the manufacture of pharmaceuticals, such as salicylic acid and derivatives, and other intermediates. In war time, phenol serves for making certain explosives.

FORMALDEHYDE

Formaldehyde, CHOH , is a gas which dissolves in water to form a concentrated solution; it is this solution which enters the market. Formaldehyde is made by the partial oxidation of methyl alcohol catalyzed by copper gauze, or other agents. A mixture of air and alcohol is provided by bubbling air through warm methyl alcohol in a copper vessel fitted with steam coils. The air-alcohol mixture passes a dephlegmator held at 40° to 50°C. (100° to 122°F.) and then enters the oxidizer. The oxidizer is a cast iron vessel with a central flue which facilitates the elimination of the heat of reaction. The gaseous mixture passes across a layer of copper filings which acts as catalyst, and which maintains itself at 550° to 600°C. (1022° to 1112°F.) by the heat liberated during the reaction. The gases leaving the converter contain formaldehyde, some methyl alcohol, nitrogen and water. They may be cooled suddenly in order to prevent side reactions; this is accomplished by passing them at once to an absorber, where a cool hydrous solution meets them, and at the same time abstracts the formaldehyde. There is formed a water solution containing 30, 35, or 40 per cent CHOH by weight, and some methyl alcohol, esters and methylal. In a second absorption vessel, methyl alcohol is retained. The outgoing gases are scrubbed for small amounts of alcohol, the weak solution concentrated in a column still, and the recovered material used in the process. The crude formaldehyde may be refined by distillation.

³¹ "Phenol made by vapor phase regenerative process," by Theodore R. Olive, *Chem. Eng. Progress*, November, 1940, with a pictorial flowsheet, p. 789-792.

³² "Synthetic phenols for resin manufacture," by Henry Howard, *Ind. Eng. Chem.*, 33, 1581

³³ U. S. Patent 1,789,071.

³⁴ U. S. Patent 2,007,327.

operating as just described, the yield lay between 60 and 65 per cent. It found that by maintaining the reaction mixture neutral, the formation of by-products is decreased, and the yield correspondingly raised. The acidity is insured by feeding a small amount of ammonia to the enteric mixture.³⁵

The explanation of the reaction is that, first, the methyl alcohol molecule is hydrogenated by the metal. Next, oxide formation by the metal takes place, and this is the function of the air. The oxide reacts with the hydrogen, removing it from the system, thus allowing the dehydrogenation to proceed further. The water formed leaves with the formaldehyde. The net reaction is $2\text{CH}_3\text{OH} + \text{O}_2 = 2\text{CHOH} + 2\text{H}_2\text{O}$.

Copper, and other metallic catalysts, two substances are poisons in the formaldehyde reaction; they are acetone and water. For this reason the methanol, furnished free of acetone as well as anhydrous, is to be compared to wood alcohol. With vanadium pentoxide as the catalyst, however, methyl alcohol with as high as 5 per cent acetone may be used, without loss of efficiency. The temperature, moreover, is only 225°C . (437°F .)³⁶; in some cases, the lower the temperature, the higher the yield.

A catalyst consisting of iron and molybdenum oxide has been found to be very effective; the molybdenum possesses directive power, while the iron has high activity for conversion. A lower temperature is sufficient.

It would seem simpler to hydrogenate carbon monoxide to formaldehyde, $\text{H}_2 + \text{CO} = \text{CHOH}$ instead of oxidizing methanol, which itself is made, at least in large part, by hydrogenating carbon monoxide. And indeed, several catalysts have been made which embody this principle. In one of them,³⁷ the natural gas made from wood charcoal is passed over a catalyst at 200° to 300°C . (392° to 572°F .) under a pressure of 10 atmospheres. The catalyst consists of the oxidizing agents vanadium pentoxide and chromium oxide on a siliceous earth, with smaller amounts of silver, zinc, cadmium and nickel deposited from their salts. Rapid cooling of the gases leaving the reactor, with a water spray, for example, gives a good yield of formaldehyde. The process allows as an alternative the passing of the formaldehyde vapors with more hydrogen to another catalyst in which the mild catalyst predominates, there to form methanol.

The reaction $\text{CO} + \text{H}_2 = \text{CHOH} - 0.7 \text{ Cal}$, is slightly endothermic; the reaction $\text{CHOH} + \text{H}_2 = \text{CH}_3\text{OH} + 27.9 \text{ Cal}$ is strongly exothermic.

Natural gas has been made the source for the direct production of formaldehyde (and methyl alcohol).

Formaldehyde as a by-product is obtained by the natural gas companies in connection with the removal of oxygen from the gas, in order to lessen corrosion. The materials removed in the process consist of formaldehyde, methyl alcohol, and other aldehyde. This source may become commercially important.

Formaldehyde is extremely reactive; its uses are correspondingly numerous. It serves as an insecticide and disinfectant (Chapter 38), as a chemical

³⁵ Patent 1,737,745, quoted through Marek and Hahn, "The catalytic oxidation of organic compounds in the vapor phase," New York, Chemical Catalog Co., Inc., 1932, p. 148.

³⁶ Patent 1,383,059.

³⁷ Patent 1,824,896.

reagent in synthesizing organic compounds, as an embalming fluid, a hardening agent for casein; its most important use from the standpoint of tonnage is for the manufacture of synthetic resins.

In 1940, there were produced in the United States, 180,884,573 pounds formaldehyde (40% CHOH) valued at 4 cents a pound.

Other raw materials for synthetic resins will be found under the proper heading, or by consulting the index.

CASEIN

Still another plastic is casein plastic, of which Galalith is an example. The raw material is casein, the white curds which separate from skim milk on addition of lactic or acetic acid, or of rennet, an enzyme obtained from the calf's stomach lining. The rennet casein is higher in ash content (10 per cent) than the acid-precipitated casein, and is preferred for the manufacture of the plastic. After precipitating the casein, there is left in the milk liquor milk sugar and albumen, which may be recovered. Much of the casein is imported, in the form of dry granules.

In order to prepare the plastic, the casein is powdered, mixed with coloring matter or a filler, moistened with enough hot water to form a dough which is then passed between heated rolls to form sheets. A number of sheets may be pressed to a block or other shape, while rods and tubes are made directly by means of an extrusion machine. The shaped pieces are placed in a solution of formaldehyde, which "sets" them, that is, renders them as hard as stone; finally they are dried in a warm closet.

The most important outlet for these hardened sheets is for the button trade. Very beautiful results may be produced by incorporating a pigment in the original mass, shaping the button, dyeing it on the surface, cutting a design which exposes the body color, contrasting with the surface color.

Casein is used for many other purposes, for example as a glue and for sizing paper.

Vulcanized fiber is presented in Chapter 22, under cellulose.

The relative value as insulators³⁸ for some of the substances described in this chapter, with some common substances for comparison, is shown below. In the choice of an insulator, such other qualities as resistance to heat and mechanical strength must be considered.

	Puncturing Voltage per Millimeter of Thickness
Fiber red	2,000 to 10,000
Phenol resins	2,550
Hardened casein plastic	6,000
Glass (common)	8,000
Celluloid	15,000
Hard rubber	15,000 to 38,000
Mica	28,000

Plioform. A new type of plastic is made from rubber and sold under the trade name Plioform. It requires no vulcanization. It offers the acid and alkali resistance of rubber and is tasteless and odorless. It is produced in all colors, in translucent and transparent form.

³⁸ In part from "Marks' mechanical engineering handbook," McGraw-Hill Book Co., 1916, p. 157.

OTHER PATENTS

U. S. Patent 1,946,040, catalyst for the nuclear chlorination of benzene compounds; same; 2,068,926, method of making artificial lumber by incorporating synthetic resin forming ingredients, such as urea and formaldehyde; 2,069,183, on a resin; 2,069,178, method of dispersing resins and composition produced thereby; 2,072,022, on making synthetic resins; 1,820,816, a cheap resin from phenol and formaldehyde; 1,753,030, a cheap resin from starch; 1,619,692, glyptal in urea composition, and a composition; 1,619,758, glyptal with mica flakes, similarly; 1,589,094; 1,806,798, a composition; 1,589,094, for making phenolic compounds in circulatory tubular systems; 1,851,754, a composition of formaldehyde by passing methanol and air in contact with vanadium pentoxide and a combustion retarder; 1,741,295, formaldehyde from methanol; British Patent 344,796, iron carbonyls removed from the methanol insures longer life to the catalyst; 1,705,495, for phenol-furfural condensation products; 1,705,493; 1,398,146; 1,398,147; 1,705,494; U. S. Patents 2,008,719 and 2,011,923, on polymerizing formaldehyde and esters.

PROBLEMS

Following the procedure for the phenol-formaldehyde resin by the wet method as in the text, what will be the weight of the produced fusible resin, if the yield is 90 per cent, and nothing is lost except the water of reaction and of solution in the hydro? 1000 lbs. of phenol are taken.

shipment of 2,500 lbs. of ester gum is made. If the ester is pure, and all trisinate, how much glycerin and how much rosin were required? The is 98 per cent, and the rosin 95 per cent abietic acid.

is required to make 1000 pounds of phenol from chlorobenzene. Let the combine 100 per cent, how much chlorobenzene is needed? In the manufacture of benzene, the chlorination of benzene leads to a 90 per cent recovery; how much in pounds and benzene in gallons are called for? The density of benzene is in the recovery of the hydrochloric acid, it is found that only 90 per cent of pint evolved is absorbed, the rest is lost; how many pounds of 22° Bé. acid collected? Answers: 125.7 gallons benzene; 885.6 lbs. 22° Bé. acid.

5. To make 1000 gallons of formaldehyde solution of 40 per cent CHOH content (density 1.128, from methanol by air oxidation, how much methanol, in gallons, is required, if the yield is 60 per cent? The methanol is made by the synthesis of CO and H_2 , which gives a recovery of 100 per cent; what weight of CO and of H_2 is required to make the required amount of methanol? Answers: 5833 lbs. CO , 833.3 lbs. H_2 .

To make the same 1000 gallons of formaldehyde directly from carbon monoxide and hydrogen, what weight of hydrogen and of carbon monoxide would be required if the recovery is (a) 60 per cent; (b) 80 per cent?

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The history of tanning reaches almost as far back as the history of man; and with it, the science of chemistry is indeed young. Yet in the past years, chemistry has furnished the tanner a new method, chrome tanning. In the older vegetable tanning, chemistry has simplified the process, furnished a partial explanation of the reactions, a wider variety of tanning agents, and methods for testing them and for controlling steps in the manufacture. With the aid of the chemical engineer, the time required for the vegetable tanning process has been shortened.

Chapter 36

Leather, Gelatin, and Glue*

Leather is the skin of animals, cleaned, and treated with oil, grease, or other vegetable matters which arrest its decay and make it more or less permanent. The latter substances are classified as tannins. Before tanning, a skin is almost entirely dissolved in hot water and there results a solution of gelatin, whereas after tanning, the skin is insoluble. If tannin is added to a gelatin solution, the gelatin is precipitated. Glue is gelatin which has been treated longer in the water; it jells less readily, but is more sticky.

The skins of bulls, cows, oxen, heifers, and calves are commonly used for the larger sizes; the last three give the more uniform and denser leather. The skins of sheep and goats, to a lesser extent those of the kangaroo and other species of seals, are used for the smaller sizes; they give the softer leathers for shoe uppers and gloves. The skin of the horse and the pony are also made into leather, but is of small importance.

With unimportant exceptions, skins may be said to be by-products of the meat industry; the animal is raised, and later killed for its meat, and then, usually, its skin is saved and sold to the tanner. If skins were a primary product, leather would be much dearer. This circumstance carries with it also certain penalties, in that the rancher for instance damages the value of the skins by branding, is less careful about insects which perforate the skin, and is at times careless in the removal (flaying) of the skin before its curing.

The skin has an upper thin layer, the epidermis, which carries in a small portion the hair follicle and the hair itself. Below this is the derma, or corium, many times thicker than the epidermis; it is the true leather-forming substance. Making leather means removing the hair and the epidermis, separating the flesh side from the under skin, and treating the corium so that it will no longer be susceptible to bacterial decay. The corium has a definite structure; untreated, it will absorb water as gelatin does; in fact it contains at least 85 per cent collagen, on a dry basis, and collagen with water is called gelatin; the tanning process renders the corium fibers water-resisting, permanent. Skins are not uniform in thickness throughout their area; the thickest part is at the butt.

* *Leather*, in collaboration with Mr. Ralph H. Wilson, Cataract Chemical Co., Buffalo, N. Y.; *Glue*, in collaboration with Mr. Harry F. Lichtenberg, consulting chemist and bacteriologist and dairy products, Buffalo, N. Y.

The skins of the seal, walrus, and porpoise have been made into a leather for many years; within the last 20 years, the skin of the shark and the ray has been utilized in making leather. The shark carries a calcareous covering over the skin, known as shagreen; this is removed,¹ from this point on the tanning is similar to that of cow hide.

Two main divisions in tanning are observed, chrome tanning and vegetable tanning. Chrome tanning is more modern and requires less time. It is used for the smaller skins, the "kips" and "skins"² of the tanner, which are made into shoe uppers. Vegetable tanning is used for sole leather and leather belting, also for the smaller skins to a certain extent; it is the longer process: four months would be rapid. Chrome tanning is also used to some extent in the production of belting and sole leather. In chrome tanning, from five to six weeks from the hide house to the warehouse is customary.

Preliminary Treatment of the Skins. The skins are received in the hide house in various conditions. Fresh skins from nearby slaughterhouses have received a treatment with salt, rubbed on the flesh side; skins from South America are sun-dried, as stiff as boards. The bundles of unsalted skins are opened; each one examined for defects, and the ends which would not make leather, such as ears and hoofs, are cut off and sent to the gelatin or glue maker. They are then scoured to remove salt and dirt. The dried skins³ are soaked longer to restore them as nearly as possible to their original condition.

Liming is next; it is done in pits flush with the floor. Hides require from 5 to 10 days to pass the pits, of which there are usually three; while in the pit, the hides are occasionally handled. The effect of liming is: *a*, to loosen the hair and epidermis; *b*, to swell the corium, which results from a division of the coarser fibers into its constituent fibrils; *c*, to emulsify or saponify the grease normally present in the corium. This effect is due partly to the alkalinity maintained by the excess of lime, partly to its hydrolytic action and partly to bacterial action. The liming for the kips and skins requires less time, 1 to 3 days. Sodium sulfide, Na_2S , is sometimes added to the liming suspension, as it acts much faster; or sodium sulfide mixed with lime and water to a thin paste is painted on the hair side of the skins, which are then folded together, and piled on the floor over night; the next morning the hair is loosened. For certain sheep hides bearing valuable wool, the paste is painted on the flesh side; the skins are folded flesh sides together, and left piled over night; the next day the wool can be pulled out as if it merely lay there.

The hide or skin is then ready to be scraped (beam-house work formerly by hand, over a beam; now in a machine with spiral knives which rotate fast against the skin which is moved in slowly). On the hair side the hair and epidermis are removed; on the flesh side any adhering particles of flesh and the under-skin. The hides are cut into butt, shoulder and bell pieces, or merely in two; they are not cut if the leather is to make belting.

¹ U. S. Patent 1,338,531.

² Hides are 25 sq. ft. in area; kips between 25 and 15 sq. ft.; skins less than 15 sq. ft.

³ Such dried hide or rawhide is durable; for instance the tabernacle of the Latter-day Saints at Salt Lake City was constructed with rawhide strips instead of nails in 1850 and is still in daily use.

machinery, for which as large a surface as possible is desired. The hides are next delimed and bated.^{3a}

Vegetable Tanning, Sole Leather and Belting. After deliming and washing the hides are ready for tanning. They are suspended from a wooden frame in a nearly spent tanning liquor and moved up and down a short distance by a mechanical rocker. The hides receive a change of liquor each time from the next stronger vat, until they are ready for the strongest tanning liquors. These are applied to the hides laid horizontally in a pit, with crushed tan bark laid on top of each; when all the hides are in, the water is run in to fill the pit. The hides remain in such liquors for periods of one, three, or more months, with several repackings. Tannin is absorbed, and adds to the weight of the leather. The period has been shortened by treating hides, liquor, and bark in a wooden drum and rotating it. On removal from these pits, which are called "layaways," the leather is washed in warm water and dried, after the wrinkles have been smoothed out. It is then stuffed with oil or grease, either by hand or by machinery. Sole leather receives only 2 per cent grease, but recent U. S. Army regulations for leather specify 5 per cent grease; belting leather 10 to 18 per cent; harness leather 20 to 30 per cent.

Tanning materials vary in tannin content from 3 per cent in chestnut to 30 per cent in the dried myrobalan fruit. The earliest tanning materials were hemlock bark or oak bark; as the forest receded the tanners moved from the modest original settlement on Manhattan Island in two principal directions. Those using oak bark moved into Pennsylvania, Virginia, West Virginia, North Carolina, and Tennessee; those who used hemlock bark moved to lower New York State, Pennsylvania, Michigan, and northern Wisconsin. Other areas have been added; in the southern states hickory wood has become an important tanning agent. In addition to the tanning materials proper, extracts are made and shipped long distances.⁴ It has been all the more welcome, as otherwise the tanner must make his own extracts. Chestnut wood extract is a liquid and contains 30 per cent tannin. Oak bark and hemlock bark each contain 11 to 13 per cent tannins; a bark from India contains 30 per cent. The quebracho tree of South America has 20 per cent in its wood; an extract is made which contains 60 per cent, a solid. The materials listed in this paragraph belong to the catechol-tannins; on heating them, the parent substance catechol, 1,2-dihydroxybenzene, is obtained; with iron salts, they give a green-black coloration. Another group of tanning materials is the pyrogallol (1,2,3-trihydroxybenzene) tannins, which on heating give the parent substance pyrogallol; with iron salts, they give a blue-black. The pyrogallol tannins are accompanied by sugars which on fermenting give rise to organic acids; the catechol-tannins have no sugar, which must be added. To the former group belong: myrobalan dried fruit; valonia, the acorn of the oak tree of Asia Minor; and American sumach, with about 30 per cent for all of these. The tanners in Great Britain rely largely on these importations.

^a Under chrome tanning.

⁴ Spent wood chips have been utilized as a source of cellulose for paper and similar products in the Bergius process (Chapter 16), for hydrolysis to sugars.

In addition to the natural tannins, synthetic tanning materials have been introduced, and applied successfully. Cresols, naphthalenes, and higher hydrocarbons are the raw materials for synthetic tannings, the "syntans". When cresol is sulfonated a sulfonic acid results; this when treated with formaldehyde condenses to form the tanning agent, Neradol D, polymerized or polycondensed dicresylmethane-disulfonic acid. It is a dark, viscous mass, which is diluted and partly neutralized before it is applied to the skins. The analogous condensation product from naphthalene-sulfonic acid is Neradol N, after dilution and partial neutralization, Neradol ND; it is polymerized or polycondensed dinaphthylmethane-disulfonic acid.⁵ Ordox G is a similar product with a higher hydrocarbon as starting point.

These agents are true tanning agents, in that after application, they cannot be washed out, and in that the leather is heavier than the hide. There are agents which penetrate the leather and become fixed, but, after washing, the original hide qualities and weight return; such agents are known as pseudotanning agents. Examples are fatty acids in organic solvents and aluminum salts.

Chrome Tanning. Chrome tanning is applied chiefly to the smaller kinds of skins; on leaving the deliming bath they are bated, in order to reduce the plumping which liming has caused and to render the grain smooth. This is done in a bath containing ammonium salts and small amounts of pancreatin (mainly trypsin). The effect of the ammonium salts is to reduce the pH of the skins and thereby their swelling. The addition of trypsin and ammonium salts is regulated so that the skins are brought to the optimum pH range (7 to 9) of tryptic digestion, and the removal of accessory hide proteins is thereby facilitated. Smoother grain and better "feel" of the final leather result. The progress of the bating is judged by the feel of the skins; skill is required to stop it at the proper time. Next the skins are pickled in a bath of dilute sulfuric acid which penetrates the structure and prepares for the chrome salt action; common salt is added to this bath to overcome the swelling action of the acid. The skins are folded together and a number of them pressed free from water; as they leave the hydraulic press, they appear dry.

In chrome tanning a salt of chromium takes the place of the vegetable tannins. A distinction is made between the one-bath type and the two-bath type. In the former the skins are placed in a wooden drum with a concentrated solution of basic chrome sulfate or chloride; the drum is rotated for 5 to 6 hours, which insures complete tanning. A quick test is to boil a small piece in water for five minutes; if the tanning is complete, the shape will not be altered. In the double-bath type the skins are drummed in a solution of sodium dichromate and hydrochloric acid for 3 hours; they turn yellow, and the chromium may be washed out. In order to fix it to the fiber a solution of sodium thiosulfate (hypo) acidified with hydrochloric acid is placed in the drum and left for 4 hours; at the end of that time, the goods are blue throughout and permanently tanned. The product from either system

⁵ "The industrial application of coal tar products," H. M. Bunbury and A. Davidson, New York: Van Nostrand Co., 1925, p. 142.

ced in a bath of borax and sodium bicarbonate; this is followed again water rinse.

commonly employed chrome liquor is made by reducing a mixture of $\text{K}_2\text{Cr}_2\text{O}_7 \cdot 2\text{H}_2\text{O}$ and H_2SO_4 in equal proportions, with glucose. Another considered the simplest and safest to accomplish this reduction, is by ing sulfur dioxide into a solution of sodium bichromate.

the two-bath system had been patented some years before by A. Schultz though modified in countless ways, it is still essentially as first proposed. amount of dichromate as $\text{Na}_2\text{Cr}_2\text{O}_7 \cdot 2\text{H}_2\text{O}$ is 5 per cent of the weight skins; to this is added an amount of hydrochloric acid insufficient to te all the chromic acid; $2\frac{1}{2}$ per cent hydrochloric acid is used, while 4 nt would be required, both in terms of 30 per cent HCl. For the second an amount of sodium thiosulfate, $\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$, twice or three times eight of the dichromate is taken. An equal weight of potassium omate may be substituted for the sodium dichromate.

the goods are dried and may then be split if required. The splits are gs made by a knife resembling a band saw, kept sharp by constant con- rith an emery wheel; the leather is fed in at a constant rate, grain side hen only one split is made, the upper piece travels on the table of the ne," the lower one drops to the floor. With thick leathers a number of may be made. Each split has the same area as the original piece, but nner. The split with the grain surface is made into shoe uppers; her may be made into furniture leather, cheaper gloves, and traveling- nings. If the leather is to be dyed, the dye is added to the fat-liquor, a subsequent bath. Logwood, in conjunction with direct blacks, is y used for black, and acid dyes ⁷ for other colors. In order to produce gloss, so-called finishes, that is, pigments suspended in binders mainly ting of aqueous solutions or emulsions of casein, albumen, shellac and , are spread on the leather, and the piece is polished by friction in l machines and then placed between hot plates.

le leather is rarely made by the chrome process because it gives lower than the vegetable tannage. Further, chrome sole leather loses its and sometimes gets slippery. Vegetable tanning increases the weight leather; chrome tanning does also, but not to any great extent; vege- tanned leather is sold by weight, chrome-tanned by area. An auto- machine measures the area in one passage of the skin; the total area l off on a dial.

TABLE 87.—Average annual production over the period 1935-1939
hides and skins.

	Average consumption	Average imports	Percentage imports, pieces
Cattle hides	21,612,000	2,580,000	12%
Calf, sheep, goat skins.....	91,982,000	67,494,000	73.4%

amois skin is made from the inner split of a sheep skin, by the oxida- fish oils in the presence of skins. The American Indians tanned the o skins by rubbing the brain into the dried skin. Velour leather is e finished on the flesh side.

TABLE 88.—Imports and exports of hides and skins, leather and leather manufacturers for 1939.

Imports		
Hides and skins	323,446,014 pounds	\$47,056,466
Leather		9,563,686
Leather manufactures, footwear, and other		6,539,179
Exports		
Hides and skins	36,164,082 pounds	\$ 4,224,345
Leather		13,041,811
Leather manufacture		10,268,166

The by-products of the tanning industry are hair, which is used in plaster, and the small trimmings of the fresh hides, which are used for gelatin or glue.

GELATIN

The animal skin, connective tissue, tendons, and the bone contain collagen; as previously noted, the corium of the skin is 75 per cent collagen on a dry basis. Bones are one-third collagen by weight. Gelatin is valuable for its power to hold many times its weight of water in the form of a semi-solid, called a gel, and for its power to retard or prevent the formation of crystals. A 3 per cent solution in water forms a jelly when cold.⁸

The skins used for making gelatin are rarely the perfect skins fit to make leather, but the trimmings in the hide house, and occasionally imperfect skins. The bones come mainly from near-by slaughterhouses and butcher shops, but also from long distances, such as heads from South American cattle; these often come with the horns attached. The horn pith gives gelatin, but not the horn proper. Hoofs yield no gelatin whatever. Sinews and tendons are suitable. Strict government regulations govern the selection of raw materials for the manufacture of edible gelatin, and require laboratory control of all the phases of manufacture. Glue is made from the same raw materials, but no government regulations apply.

The water employed in the preparation of gelatin must be as cool as possible in order to prevent excessive hydrolysis and the loss of jellying power which accompanies such hydrolysis. An advantage results from pre-treatment of bones and skins with lime, for the preparation of the gelatin is easier, the temperature of 65° C. (149° F.) is warm enough, and the period required is shorter. Glue may be considered as gelatin which has been hydrolyzed further; its jellying power is low, also its water-absorbing power (imbibition), but its adhesive power is greater than that of gelatin.

Bones are first freed from grease by heating them with steam under pressure, releasing the pressure to a few pounds just before opening the kettle; the grease floats on the water and may be run off. It is utilized in soap making. A better way is the extraction by means of a low-boiling petroleum naphtha, because there is no loss of gelatin-forming substance by this method. In many plants the bones are transferred over a belt conveyor which passes over a magnetic separator, placed at the turn of the belt. The bones drop off into a chute leading to squirrel-cage disintegrators where they are crushed, while any iron present is carried a short distance on the underside of the belt and then drops off into a receptacle. The crushed bones are

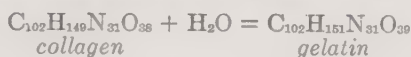
⁸ Gelatin with pH = 4.6 acidity has maximum jellying power; above or below, it is less.

led to the top of a central tower by a bucket elevator and delivered through chutes to any one of a number of tanks. These tanks may be of various sizes; large ones are 20 feet in diameter and 5 feet deep; four tanks in a battery and are operated in series on the countercurrent principle. Dilute hydrochloric acid (5° B \acute{e} ., 7.15 per cent HCl) meets the most exhausted bones, while nearly spent acid overflows into the tank containing the fresh bones. The mineral matter of the bone, mainly calcium phosphate and carbonate, dissolves, leaving the organic matter, the collagen, with the original shape of the bone. Collagen so prepared from bones is called ossein. It may be treated further at once, or shipped to a factory. The latter procedure is sometimes economical if the ossein plant is located near a heavy chemical plant, so that the hydrochloric acid can be pumped through glass lines directly into the ossein plant, avoiding the rail transport of acid. Skins do not need the preliminary acid treatment since their color is not masked by mineral salts.

The ossein is placed in 5-foot cubical concrete vats, of which there are several hundred, with slaked lime and water, and left there for a month or more. The ossein swells and turns snow-white; the mucins and albumins are dissolved, and any remaining grease is saponified. At the proper time,⁹ the ossein is removed to a rotary tank and washed with four changes; first with water, then with dilute hydrochloric acid, then twice with water; the whole in the washer is one day. The ossein is then ready for extraction. Skins are treated in the same way; they become translucent.

The extraction of the limed ossein or skins is performed in tanks 4 feet in diameter and 4 feet deep, with a steam coil under a false bottom; the charge is on the false bottom and thus does not come into direct contact with the liquid. The water is maintained 60° C. (140° F.); in 8 hours a first extract containing 8 to 10 per cent gelatin is formed; it is filtered and cooled. A second extraction is made at 65° C. (149° F.); a good strength is obtained; the liquor is filtered and cooled. A third extract is made at about 75° C. (165° F.), but this will be too weak to jelly on cooling, so that it is concentrated in a vacuum to the jellying strength. The third run is darker and has less jellying strength; it is still edible, but is used for its water-retaining property chiefly, in marshmallow confectionery, for example.

The reaction which takes place during extraction is probably as follows:



The filtration of the warm gelatin solution is done in a special circular filter shown in Figure 198; the filtering medium is wood pulp; the solution flows from the entering space near the shell to the central channel. In order to keep the central channel a considerable layer of wood pulp must be maintained; here the solution deposits the suspended particles, which cause turbidity. The gelatin solution from the filter is placed in long steel molds 6 inches deep and 6 inches wide, and cooled in refrigerated rooms. The resulting solid jelly is removed from the mold and cut by hand into one-half inch by 2 inches and 6 feet long. These are laid on Monel

if the liming is continued too long, ammonia is evolved, and the material is spoiled.

metal wire set in frames, stacked on small trucks and shoved into tunnel 70 feet long through which filtered air heated to 40°C . is pulled by exhaustor. The gelatin strip dries to a thin sheet which still contains about 10 per cent of moisture; this amount is not removed. The strips are usually ground to a coarse powder for greater ease in handling.

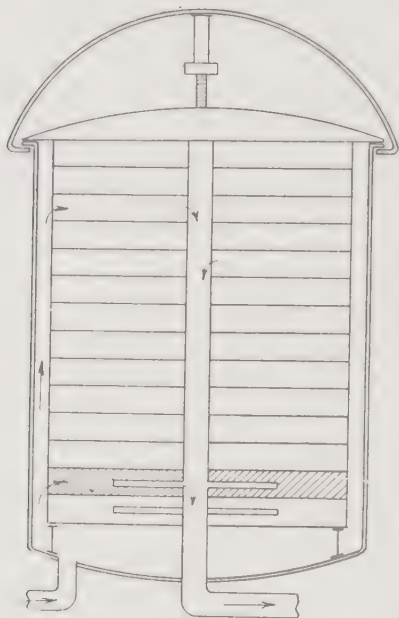


FIGURE 198.—Filter press for gelatin solution.

In some factories the filtered and partially cooled gelatin solution is coagulated on the surface of chilled, revolving drums from which it is discharged in the form of a sheet onto a moving belt. The latter passes slowly through a drying tunnel from which dry, hard and transparent sheets emerge. The sheets are then ground to a powder.

Uses of Gelatin. Gelatin is a food accessory, easily converted into amino acids in the stomach; it is valuable also mixed with other foods because it disseminates the particles. With fats and oils it forms an emulsion which greatly facilitates the digestion; hence its use with meats and in dessert. Its use in ice cream is due mainly to its function as a protective colloid; it prevents the formation of crystals of lactose sugar and water during the storage period, at the temperature of -10°F .; the proportion of gelatin sufficient for this result is 0.5 per cent. About 3000 tons of gelatin are used per year in the United States for this purpose. Its use in confectionery has been mentioned. All these uses together account for a yearly consumption of over 10,000 tons of edible gelatin in the United States.

Gelatin is used for capsules in the pharmaceutical houses; the hard two-piece telescopic capsules are gelatin alone; the flexible capsules contain glycerin also. In the manufacture of photographic plates, films, and moving-picture films, gelatin is used for the sensitized coating which holds the silver salts. It has many other minor uses.

When gelatin is made from bones, there may be obtained as a by-product dicalcium phosphate, or by using more lime, tricalcium phosphate;

is used as a fertilizer, the latter in the potteries for "bone china." Calcium chloride is formed at the same time, and is usually wasted. Calcium chloride as a by-product has been mentioned.

GLUE, AND "PELLET GLUE" PROCESS

The manufacture of glue is identical with that of gelatin, except that the materials need not be selected with such care. The extraction of the stock (ossein, lined skins) may be performed in a single "boil," but extractions of shorter duration are preferable; the liquor is concentrated to perhaps 15 per cent in vacuum condensers. This concentrated solution is congealed in thin layers, and these are dried in a tunnel drier. A preservative is added to the concentrated solution (borax, formaldehyde); this cannot be done for edible gelatin.

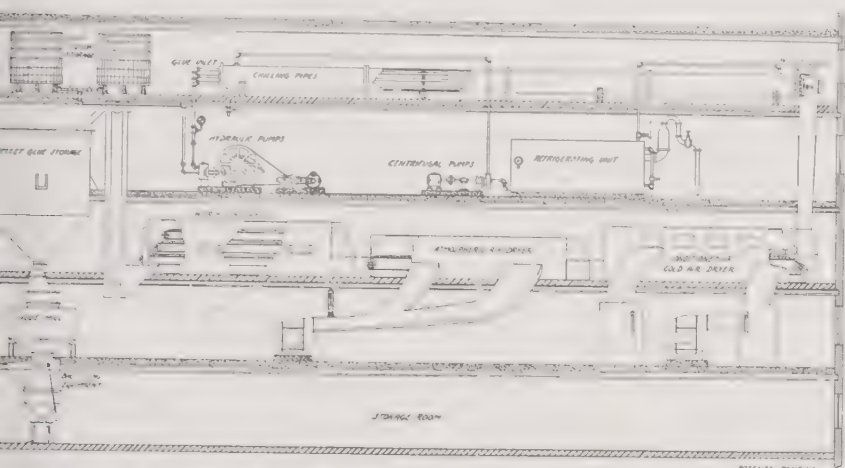


FIGURE 199.—Lay-out of a pellet glue plant. (Courtesy of Darling and Co., Chicago.)

Instead of drying the chilled strips of glue in tunnel driers, a method was devised by Thomas K. Lowry, in which pellets of glue are formed in a continuous process, eliminating the tunnel drier and all the labor it involves.¹⁰ The 50 per cent glue solution is chilled, and forced through wire grills; a revolving knife cuts off (scrapes off) the protruding strips into small pellets of equal size. The pellets pass through a three-stage system of drying. The first stage operates at 70° F. In this drier the pellets are kept in constant motion by automatic rakes. In the second stage the temperature is 100° F., and in the third, up to 130° F. Pellet sizes vary from $\frac{3}{16}$ to $\frac{3}{8}$ inch. The time in the first drier is 3 hours, in the second 6, and in the third 9. The total time is therefore 18 hours, instead of the 2 to 6 day period required by the older method. Figures 199 and 200 will help make the procedure clear.

Another method involves dropping the glue pellets into hot toluene. The removal of grease from glue is essential, because it interferes with

the adhesive power. A practical test is to make a 5 per cent solution, add a water-soluble dye, and paint this on a white board. Examination with a hand lens will reveal white spots if grease is present.

A strength test is made by gluing together two wooden blocks and after definite time, placing them in a machine which measures the force required to pull them apart.¹¹

Animal glue of the best quality is still unsurpassed for strength; it is used in furniture making, in veneering, book-binding, rug-sizing, in making

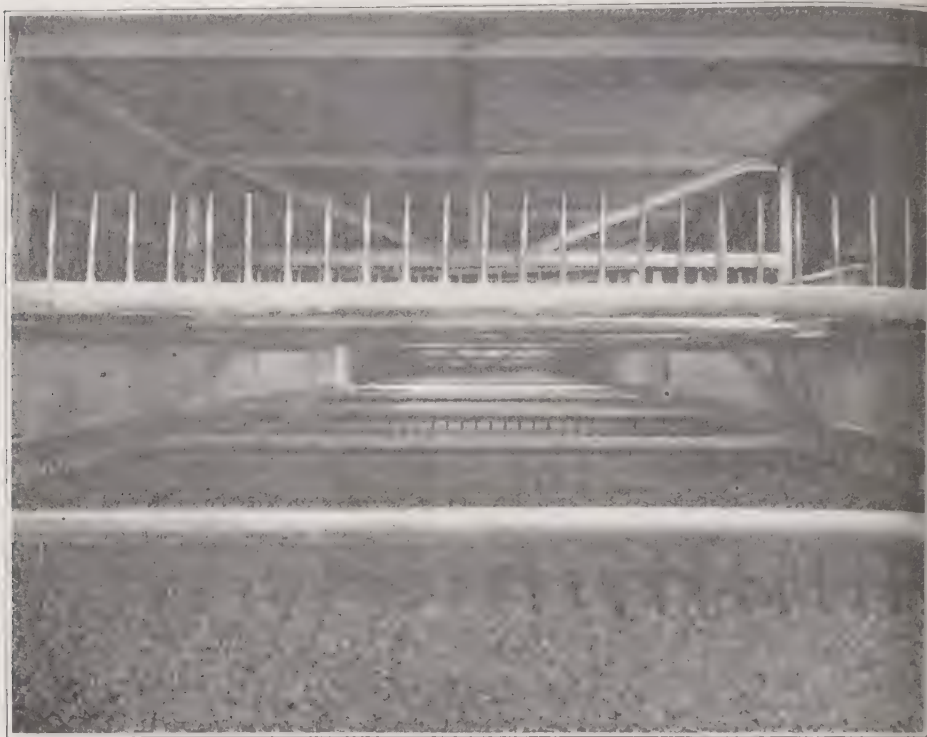


FIGURE 200.—The Thomas K. Lowry process for producing glue in the form of dry pellets. First stage drier, operated at 70° F., with rakes on an endless chain. (Courtesy of Darling and Company, Chicago.)

the tips for matches, in sizing straw hats, for making sand paper, emery, Carborundum, and other abrasive papers. With waste leather, it makes imitation leather; ground cork is made into shapes with glue. A waterproof animal glue is made by adding tannins or formaldehyde.

Other Adhesives. Fish glue is made from the skins of the cod, eusk, and other fish; the washed material is heated with water and concentrated phenol may be added and a little oil of wintergreen (synthetic) in order to mask the odor. Isinglass is the dry glue made by boiling the air-bladder of the sturgeon.

Fresh casein boiled with water has adhesive properties; once set, moisture does not weaken it. Starch paste or British gum is made by digesting starch with dilute acids. A solution of sodium silicate is an adhesive; it is called

¹¹ Glue has maximum strength when its pH is 7.0; glue contains considerable calcium carbonate, calcium gelatinate.

g. but sets quickly, and is valuable in the manufacture of cardboard and corrugated paper. Mucilage is a solution of gum arabic or acacia in water. Marine glue is merely a name for a waterproof adhesive containing rubber, shellac, and naphtha.

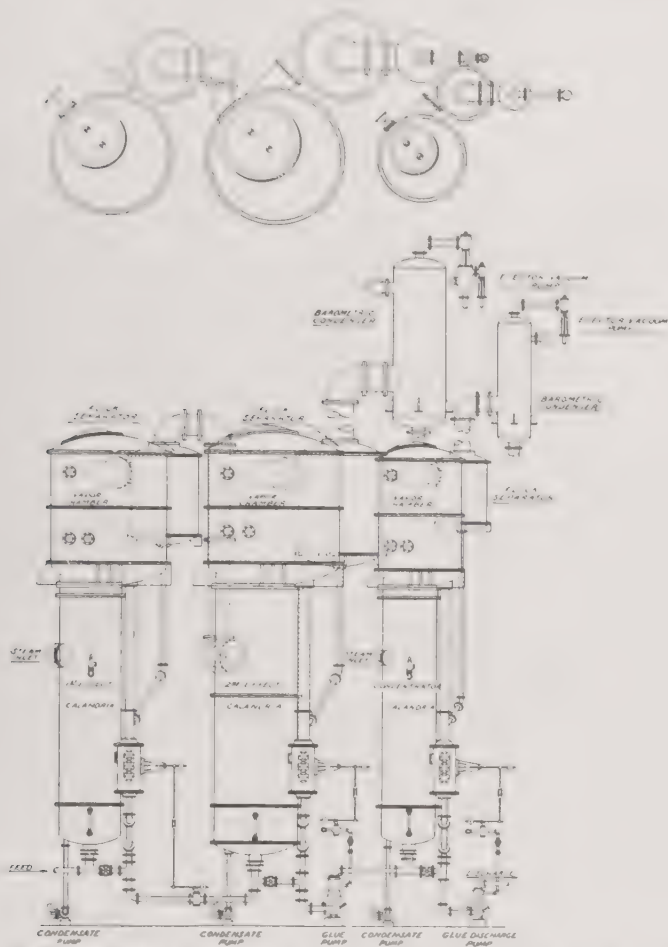


FIGURE 201.—A W&S continuous glue evaporator with a double effect evaporator followed by a concentrator, High Velocity, Long Tube, One Pass, Climbing Film Type. Note from the plan the tangential connection from vapor chamber to Flick Separator. The three vessels differ in size to meet the changing conditions of gravity and viscosity of the liquor. The high vacuum provided permits the use of comparatively low temperatures; the period of heating is short, the liquor passing through the unit (all vessels) in 10 minutes. (Courtesy of Wurster and Sanger, Inc., Chemical Engineers, Chicago, Illinois.)

Theory of Tanning. The study of tanning, and of the nature of glue, is an important branch of chemistry called Colloidal Chemistry. It includes in its considerations the combinations due to forces between particles, and at those surfaces, such as droplets, grainlets, or bubbles of microscopic dimensions, in a gas, liquid or solid; pure chemistry concerns itself primarily with forces and events within the atoms and molecules, and

TABLE 89. *Production figures for glue and gelatin in the United States (1931).*¹²

	Pounds	Value per pound
Gelatin		
Edible	22,373,480	32.6 cents
Inedible, photographic	6,770,745	48.6
Glue		
Hide and extracted-bone	63,983,949	12.7
Green-bone	37,108,168	8.05
Vegetable	178,474,477	5.05
Casein	10,239,221	11.2
Flexible and fish	14,588,017	15.85

* Bureau of the Census.

between them. For the combination of tanning agents with the collagen corium a simple reaction cannot be written. In the tanning process, tanning agent is more or less irreversibly fixed by the hide protein where its hydrophilic centra are changed into hydrophobic (dehydrating, water repelling) groups. Resistance of the product toward the action of proteolytic agents is thus acquired.

It was the substance glue, the first one studied with respect to surface forces, which gave its name to the branch of the science.¹²

OTHER PATENTS

1,848,506, thiophenol tanning and mordanting agents; 1,851,021, producing water-soluble tanning agents which comprises condensing a methylol compound of a methylic phenol with resorcinol at a temperature below 50° C., in the presence of water and a condensing agent; 1,844,018, a new tanning composition comprising the hydrogenated reaction product of sulfite cellulose and hydrogen peroxide; 1,895,446, process for producing a transparent clear bone glue or bone gelatin solution; 1,895,433, improving water-resistance of casein glues, by treating with a polymerized acetaldehyde; 1,858,193, manufacture of vegetable-tanned sole leather; 1,881,763, process for dressing and drying leather; 1,753,694, leather finishing compound consisting of emulsions of oil, sweet oil, cod liver oil and glycerin; 1,744,756, a leather-stretching and tacking machine; 1,892,599, a process for the manufacture, sterilization and puffing of gelatin; 1,310,148, apparatus for stretching and drying leather.

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¹² The Greek word for glue is kolla.

Photography plays an important part in modern life; it serves not only scientific photography, such as portraits and landscapes, but for numerous artistic and medical purposes. It serves the armed forces in a variety of ways. The photographic film is superior to the human eye in that it is sensitive to wave-lengths of light to which the former is insensitive. It is to photography that we owe the inexpensive entertainment of the moving pictures.

Chapter 37

Photographic Plates, Films, and Papers; Lithography

Photography has passed through several stages on its way to its present position of almost universal service. Originally developed as a means of recording stage settings (Daguerre), it became a replacement for painting, a hobby. With the introduction of gelatin and later of the flexible film, the present dry plate and rolls of film became possible, and photography improved more and more, allowing exposures of very short duration, and finally reached their present state of perfection. Pictures of landscapes, perfect and sharp, are taken as a matter of routine from airplanes moving 100 miles per hour, with exposures of one three-hundredth second.¹ Photography relies for its evidence on photographic records of the position of objects and of their motion.² The microstructure of metals and alloys is revealed by photography. The absorption of light in the ultraviolet (shorter wave-lengths than blue) and infrared (longer wave-lengths than red), to both of which the eye is insensitive, is revealed by photography. The selective absorption of x-rays by teeth, bones, metals, and coated animal skins gives opportunity for photographic records indispensable in modern medicine and surgery. Portraiture has become a fine art. In periods of warfare, the camera with a telephotic attachment, operated in an airplane, observes in an instant more than the human eye could in an hour, and transmits information, independently of memory, in a way which allows for ready study. A valuable contribution was also made in developing the lantern slide and film pack, which may be introduced and removed from the camera in full daylight; it has greatly stimulated amateur photography. The crowning social achievement of photography is the life-like motion picture. The making of the talking pictures in which sounds are recorded and reproduced photographically.

The uses of photography listed above depend upon the action of light on silver bromide, with a certain amount of iodide admixed. In blue prints, potassium ferricyanide and expensive iron salts are used, and the development is simple and rapid. For that blue prints have become the means of recording drawings and reproducing them of all kinds.

The present dry plate and dry film were preceded by a plate which was developed just before using, and without drying (wet plate); this method is

County, N. Y., has been photographed from the air, so that a complete map showing roads, bridges, and buildings is available; the elevation of the airplane was 9500 feet.

Einstein's theory that light is deflected by astral bodies is tested photographically; also the prediction of an eclipse.

still useful in certain branches of commercial work. Still another method of photographing depends upon the hardening action of light on albumen containing sodium dichromate, and this principle is applied on a large scale in lithography by the zinc plate method.

The Light-sensitive Emulsion. For dry plates, films, and (silver) paper, the light-sensitive part is the coating of gelatin in which silver bromide crystals with some silver iodide crystals are disseminated; the gelatin coating is the essential part, the glass plate, the flexible film, or the paper furnishing merely a suitable support.



FIGURE 202.—X-ray picture of a tulip. Note the vein structure in petals and leaves. (Photographed by M. C. Reinhard, M.A., Buffalo, N. Y.)

The gelatin used is made from calf skins.³ A solution of potassium bromide with some potassium iodide is prepared, to which 3 per cent gelatin is added, and to this solution, a lukewarm water solution of silver nitrate is added; the silver bromide which forms remains in suspension by virtue of the protecting action of the gelatin. After the silver nitrate solution has been added, and in some plants after "ripening" (as explained further), the gelatin content is raised to 7 per cent. This strong gelatin suspension, really a colloidal solution, is commonly called the "emulsion"; it is cooled to a soft jelly,⁴ and made into "noodles" which are placed in water for the purpose of removing the potassium nitrate formed as the second product of the reaction $\text{AgNO}_3 + \text{KBr} = \text{AgBr} + \text{KNO}_3$. If the ripening process has not been performed with the 3 per cent gelatin, it is performed with the

³ Chapter 36.

⁴ There is no difficulty in obtaining a jelly; for even a 3 per cent gelatin solution forms a gel at room temperature.

at gelatin, before washing. Instead of water, a solution of calcium is used for washing, because the latter does not swell the gelatin as water would. The excess potassium bromide is dissolved as well as potassium nitrate formed.

ripening. In order to raise the sensitivity (speed) of the emulsion, it is ripened at 32° C. for 6 to 7 days, or at a higher temperature; the heat causes the gelatin to lose its jellying power, and for that reason, the 3 per cent solution is heated, and fresh gelatin added at the end. The proportions of bromide and iodide (34 of the former to 2 of the latter) to silver

FIGURE 203.—Pyelogram, an x-ray picture showing the ureter and the kidney cavity, by injection of 15% sodium iodide through the bladder. (Courtesy of M. C. Reinhard, M.A., Buffalo, N. Y.)



are greater than required for the reaction, so that there remains an excess of potassium bromide; this must not be removed before the ripening, for without it, no ripening, or increase in the sensitivity takes place. The period is regulated according to the degree of sensitivity desired, and increases with the time of heating; but there are other factors which regulate speed. The greater the proportion of silver salts to gelatin, the faster the plate; furthermore, silver bromide alone is more sensitive than silver bromide with iodide addition. It is not uncommon to blend various emulsions of emulsion. If the ripening is at a moderate temperature, the power of the gelatin is not impaired, and the ripening may be performed with the 7 per cent gelatin. There are many modifications of the process just described.

A warm emulsion is then placed in cheese-cloth bags, and pressed under heat; the stringlets of emulsion coagulate and form a product resembling a plate. A fast plate requires a short exposure only; a slow plate, a long exposure; in the usual emulsion, silver salts are 30 per cent of the total.

ling noodles. These may then be washed in the cold calcium sulfate solution mentioned before, without dissolving; only the water-soluble salts are not wanted pass out in the water.

The washed gelatin in noodle form is remelted, and there are added at this point some alcohol, a very little thymol as a preservative, chrome alum, and some potassium bromide as a retarder; all these substances are in solution. The alcohol helps the flow of the emulsion, and the chrome alum hardens it. The emulsion is now ready to flow onto the glass plate or film, and is allowed to set by cooling. For the films especially, a preliminary undercoat is advisable, which will bind the emulsion sheet to the pyroxylin; it consists of gelatin solution with chrome alum and potassium bromide. The film may be double-coated, and the grain made exceedingly fine.

Plates and film⁶ are then dried in a current of warm, dry, filtered air. Photographic paper is coated in the same way as plates and films, but as a rule, the emulsion for plates and films is much more sensitive than paper. A specially made paper is coated with a white pigment, usually barium sulfate, then examined for defects, and finally coated with the light-sensitive silver salt emulsion, generally in albumen. For enlargement paper more sensitive than the usual contact paper is made. Making the emulsion, ripening it, coating plates and films as well as paper, and drying must be performed in a dim red or orange light.

Camera. The plate is exposed in the camera (plate holder) which for short exposures must have a lens allowing maximum light to enter, and a good shutter. Improvements in lenses and shutters have kept pace with advances in plate and film manufacture. For moving pictures a special camera is obtainable for amateur use (with 8- or 16-mm. film, instead of standard 35-mm. width).

Developing and Fixing. The exposed plate (or film) is placed in an alkaline developer in the dark room; the developer causes metallic silver to form at the spots affected by the light, the depth of the silver deposit being proportional to the intensity of the light. After the picture has appeared and has begun to disappear, the plate is removed from the developer, washed with water, and placed into a solution of sodium thiosulfate (Chapter 4), which removes the unchanged silver salt, thus fixing the image. After washing, the plate is dried, and is now the negative. From the negative, a positive is printed on paper.

The alkaline developers are hydroquinone, $\text{HO} \langle \text{benzene ring} \rangle \text{OH}$, pyrogallol, 1,2,3-trihydroxybenzene, methol, or methyl-para-aminophenol, $\text{OH} \langle \text{benzene ring} \rangle \text{CH}_3$, in the form of sulfate, and eikonogen, the sodium salt of α - and β -naphthosulfonic acid. These are called alkaline developers because they are used in a solution of sodium carbonate. Sodium sulfite is also added to prevent oxidation by the air, and a little potassium bromide to retard development of the unaffected silver bromide. Amidol is used without alkali; it is diaminophenol hydrochloride, $1,3,4\text{-C}_6\text{H}_3 \cdot (\text{OH})(\text{NH}_2)(\text{NH}_2)\text{HCl}$. One developer may give a green shade, another a brown shade of black. As a rule, a mixture of two developers is used to give deep blacks.

⁶ *Tariff Information Survey*, N25 (1921).

moving pictures, it is convenient to make a negative, from which number of positive films may be produced.

Explanation of the action of light on the rapid photographic plate is as follows: In the silver bromide lattice (which makes up the grain itself embedded in the gelatin) there are sensitive centers due to the presence of silver sulfide molecules. Wherever there is present a silver sulfide molecule, the normal lattice is distorted, for Ag_2S does not fit into the normal AgBr system. At each place of distortion, an exceedingly slight impulse will suffice for the liberation of a free silver atom, whereas a quantum of energy thousands of times greater would be required to liberate a silver atom from the normal, undistorted silver bromide lattice. Translated into photographic terms, the distorted lattice results in a fast plate, while the undistorted lattice makes a slow plate or paper (such as the old *print-out paper*).

Silver sulfide has its origin in an impurity of the gelatin, present in very minute amounts, called allyl mustard oil; this substance reacts with silver bromide to form, after several intermediate compounds, silver

invisible latent image consists of a minute amount of metallic silver. A slight amount becomes the nucleus for further deposition of such silver as the developer produces from the silver bromide.

A photographic dry plate prepared from the gelatin emulsion of silver bromide is sensitive to wave-lengths in the green, blue and violet, the region between 400 $m\mu$ to 400 $m\mu$. By adding a dye such as erythrosine, ethyl red, pinachrome, or orthochrom, to the emulsion, the resulting plate or film becomes sensitive to yellow, as well as to green, blue and violet; such plates are called *orthochromatic*. By the use of polymethine dyes, plates sensitive to the whole visible spectrum are produced, and are known as *panchromatic plates*. For photographing in the infrared, in the region between 700 and 800 $m\mu$, eosin or cyanine is the dye added to the emulsion; for the region beyond 800 $m\mu$, as far as 1014 $m\mu$, a plate sensitized with neocyanine will record the image. In this fashion, the photographic plate can reveal light waves invisible to the eye, and longer in wave-length than red light.

In the ultraviolet, good records are obtained with panchromatic, or *ultraviolet* plates in the region between the violet and 320 $m\mu$. Below 320 $m\mu$, or at 200 $m\mu$, the plate may be made sensitive by covering it with a layer of petrolatum, so that the invisible light of wavelengths shorter than 300 $m\mu$ may also be caught by the photographic plate.

An additional striking advance has been made. After a highly sensitive plate has been exposed, it may be bathed in a solution of phenosafranin, with the result that its sensitivity to light is reduced so considerably that it may be developed by ordinary lamplight, with perfect results. This is called *reducing*.

Plate Process. The wet plate process is older than the dry plate, and is still used for commercial work, such as in lithographic plants. The plate can be used over and over, after the negative is no longer needed. The plate is coated with collodion (pyroxylin dissolved in ether-alcohol) containing potassium bromide and some iodide, dried for a few moments, and bathed

in a solution of silver nitrate; the excess solution is allowed to drain off the plate is ready for exposure. It is developed by means of a solution of ferrous sulfate in dilute sulfuric acid; the negative image appears as metallic silver as with the dry plate. The unchanged silver bromide is removed by a dilute potassium cyanide solution. The negative may be intensified by means of copper sulfate and potassium iodide solution, followed by silver nitrate. Finally a solution of sodium sulfide converts the image to a jet black.

In dry-plate photography, a faint negative may be intensified by means of a solution of bichloride of mercury followed by ammonia; a picture which is too dense, on the other hand, may be reduced by means of ammonium persulfate; there are several other formulas.

COLOR PHOTOGRAPHY

Transparencies in the natural colors may be obtained by photographing on the several plates available, that of the Lumière brothers is the easiest to handle. It consists of a glass plate coated with a layer of starch granules of three colors, violet, red, and orange; over the starch layer, the sensitive gelatin layer is placed. The plate is exposed glass side out, so that the light must pass through the granules before reaching the gelatin. A single flower for example would send its rays through red granules, behind which the silver bromide would be affected. On developing, only these particles of silver bromide would change to metallic silver. The procedure at this point is different from that for ordinary negatives, for the picture is reversed. It follows: After washing in water, the deposited silver is removed by a solution of potassium permanganate in sulfuric acid. As one looks through the plate the red granules forming the flower are now clear; it is now necessary only to block all the other granules. This is done by taking the picture into daylight, immersed in the original developer. The unchanged silver bromide is changed to metal, permitting no light to pass, so that only the image of the red flower appears on holding the plate against the light.

Color films are in process of development. Color plates and films are used in medical studies.

LITHOGRAPHY

The word lithography has come to mean the printing from stone or metal in several colors, partly superimposed to reproduce an original artist's painting. Metals are used in rotary presses. Either aluminum or zinc sheets are employed; they are used over and over again, but the surface must be suitably grained before application of the printing image. Stones are no longer used, except for small work and special studies. The preparation of the metal plate images is largely a photographic process. It is appropriate to discuss lithography in this chapter for another reason: the first utilization of the action of light on chemicals was in lithography (Niepce), preceding photography proper.

In stone lithography, fine-grained limestones (from Bavaria) are covered by hand drawing, with the lines and areas of a single color. The stone is then treated with dilute nitric acid for a brief period, which attacks the un-

portions, leaving the greased portion slightly raised. The stone is in a back-and-forth press, and touched at one end by a water-wet further on by an inked roller (paint); the bare stone is moistened, only the greased portions take the ink.

In the zinc-plate process, the single colors are selected not by the human eye but by the camera. The original artist's painting is photographed three or more times, each time through a screen which blocks off one color, but allows the others to reach the gelatin plate; to make this point and the others clearer, a yellow flower may be selected. The first picture is taken through a violet screen which stops yellow but allows blues and reds to pass; hence the flower will be represented in the developed and fixed plate by clear glass (1). A positive is now made, through a screen of fine lines (diamond-shaped openings, with 133 lines to the inch); the image obtained is in the form of dots, which allow gradations in intensity. This positive is on ground glass, and is retouched; the yellow flower is retouched by a deposit of silver, while the rest of the plate is clear glass. A second negative is made (3), again retouched, and used finally for the production of the zinc plate (4). In the second negative, the yellow flower is represented by clear glass, so that the positive made from it, on the zinc plate, receives a flood of light wherever there is yellow in the original painting.

The zinc plate is coated with a solution of albumen containing ammonium dichromate; the solution is spread evenly by tipping the plate; after drying with a small electric fan, the plate, hung vertically, is ready for exposure. It is exposed under negative (3) in the special movable arc exposure frame. The size of the zinc plate varies, but is perhaps 4 feet by 3 feet; the plates are of various sizes, but frequently of the size of a magazine cover. The zinc plate is large enough to accommodate a number of images, sometimes as many as 25 or 30. The albumen-dichromate layer becomes insoluble under the action of the powerful arc light. The exposed metal plate is laid on a table in the dark room, and covered completely with a liquid wax containing a black pigment. Cold water is flushed over it while a turntable rotates it around; light pressure from a sponge helps remove the unaffected portions of the albumen, while the affected portions remain and are now exposed. The developing over, there remains only a treatment with chromic acid and phosphoric acid, and gum acacia.

The zinc plate is mounted on the cylinder of a rotary press, and moistened with water by one roller, while another roller presents the ink or paint; the water takes the water, but the waxy surface of the image repels it; the ink, on the other hand is repelled by the wet metal, but is received by the image. On being pressed against the paper, the yellow flower is printed in yellow ink with the exact gradations in intensity. In a second plate for the red will have been prepared, and will print, on the paper already bearing the yellow portions of the picture, whatever was red in the original painting; in a third, the blue will be applied. A fourth with green and a fifth with the black are common, and the number runs as high as ten with a corresponding increase in beauty and also in cost.

Printing from zinc plates bearing several images is called multiple

printing; the roll makes 3000 to 3600 r.p.h. and for each revolution, with perhaps 25 images is inked.

In the "deep-etch" process of more recent introduction, the zinc is coated with a special gum-containing coating, and exposed under a negative. The unexposed parts are cleared by means of a hydrochloric acid solution containing zinc chloride. The bare metal is etched, and impregnated with ink; this is the image which will print in the press. The unprotected parts of the coating are now removed, and the metal surfaces descaled by gum acacia and nutgall solutions. In the "deep-etch" plate, the image, hence the image, is seated on the metal, just as in the old "transfer" process; there is no film of albumen to wear away. It has been deservedly successful.

The value of photographic materials such as plates, moving picture film (unexposed) and other films, paper, chemicals for developing and fixing, exceeds 40 million dollars per year, for domestic production (U. S.). Cameras, including motion picture cameras, were \$4,604,479; films, motion picture and others, \$40,899,597; sensitized paper, \$13,622,206; plates and slides, \$944,717; total photographic apparatus, materials, and supplies, \$69,874,994, all in 1935 (U. S.). In 1941, the total was 77 million dollars; in 1939, it was 111 millions.

Blue Prints. The light-sensitive paper used for blue prints consists of white paper coated with a solution of ferric ammonium citrate and potassium ferricyanide; the coating is done automatically, in rooms with subdued light. An India ink tracing on cloth supported by a coat of pyroxylin is placed between the sensitized paper and the source of light; the black lines penetrate the coating, but elsewhere the iron of the citrate is reduced (from ferric to ferrous). On immersion in water, the unaffected mixture dissolves while the reduced iron forms the insoluble blue ferro-ferricyanide⁷; the fixing agent is merely water. The result is a design of white lines on a blue field. Strong light must be used, such as direct sunlight for 15 minutes; ultraviolet lights are the modern practice in plants requiring many blue prints. Similar papers are available which give blue lines on white ground, or pink lines on white.

Of increasing importance is the process known as photostating, in which the page of a book, print, or picture is reproduced as a paper negative by the reflection of strong light; the negative may then in turn be illuminated and made to produce a positive. The paper used is a silver bromide paper. No plate nor film is necessary.

OTHER PATENTS

U. S. Patent 2,005,837, manufacture of photographic emulsions; 1,991,136, photographic emulsion; 1,787,564, manufacture of fire-proof photographic films; 1,890,490 and 1,890,490, apparatus for propelling long strips of films, such as motion picture films, through a liquid bath; 1,815,513, manufacture of films from an aqueous emulsion; 1,889,818, apparatus for developing photographic films; 1,860,059, apparatus for developing roll films; 1,742,814, machine for assembling photographic films; 1,820,593, lithographic printing machines; 1,820,593, lithographic plate and process of preparation.

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⁷ Ferri-ferricyanide is not blue, but brown-yellow, and soluble in water.

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Chemical fertilizers play an important rôle in increasing the crop of grains and cotton. In another way, chemical science has made itself indispensable to the agriculturist, in the killing of insects which render fruit wormy or destroy the foliage, and in the control of fungi which destroy the fruit and destroy the trees or vines. Such crops as the potato, tea, and cotton are all subject to pests which are successfully fought by means of chemical poisons.

Chapter 38

Insecticides, Fungicides, Disinfectants

The application of chemical substances below the soil provides the plant with extra food which permits better growth resulting in a greater yield per acre; but above the soil, the plant also stands in need of the products of chemical science, in the form of insect killers (insecticides) and fungicide destroyers (fungicides). The apple tree alone, for example, is subject to the following insect pests: the codling moth, the San José scale, the apple red bug, apple and thorn skeletonizer, bud moth, apple maggot, gipsy sawfly, canker worm, and nine more.¹ In addition it is subject to fungous diseases such as the apple scab, cedar rust, and several others. The proper choice of chemicals is determined by experiments performed at State and Federal experiment stations, and the knowledge so obtained is offered free to the agriculturist. The method of application is by spraying a suspension of the chosen materials in water, or by "dusting" the powdered dry material. In general spraying is better, and more widely practiced. The system of protecting crops in this way has become of great importance and wide application, so much so that unsprayed fruit is essentially unsalable. The most important substances employed are lead and calcium arsenates, lime-sulfur, Bordeaux mixture, kerosene and other emulsions, and powdered poisonous plants. For certain diseases such as the fire blight, a bacterial disease (apple tree), the remedy is to cut off the affected branches and twigs in the wintertime, and to disinfect the cuts with a solution of mercuric bichloride (HgCl_2). The destructive insect pests are held in check also by birds, toads, beetles, and parasitic insects; other means of protection are banding the tree trunks with sticky materials to prevent the ascent of caterpillars and wingless moths, band traps, and local application of the fire torch.

INSECTICIDES

The agricultural insecticides may be divided into three classes: (1) the stomach poisons, for insects which eat the foliage; these include arsenate of lead, arsenate of calcium, hellebore, and paris green; (2) the contact insecticides, effective against insects which do not eat the foliage, the borers and beetles; to this group belong lime-sulfur, nicotine dust, and kerosene emulsions; (3) the fumigants, used against borers which are not reached by sprays, and for the protection of grain stored in warehouses; some of the substances in this class are carbon disulfide, hydrocyanic acid, ethyl acetate

¹ "Injurious insect pests and fungous diseases," N. Y. State Dept. Farms and Markets Cir. No. 13-10 (1925).

tetrachloride mixture. The divisions are not strict, for one substance may fall in two classes.

Stomach Poisons. The production of lead arsenate, calcium arsenate, Paris green depends upon arsenic, usually arsenic trioxide or white arsenic, and a discussion of their manufacture will of necessity include a discussion about the availability of arsenic trioxide.

White arsenic, As_2O_3 , is a by-product of the smelting of copper and lead; it is carried out with the fire gases and may be collected in settling chambers, cyclones, filters, or in the Cottrell electrical² precipitator. The removal of arsenic dust is obligatory in many states, so that a certain source for white arsenic is assured; it is, however, also obtained by roasting arsenic sulfide and other ores, in which operations it is the primary product. When copper smelters work to capacity, the Anaconda smelter (Montana) can supply 10,000 tons annually from its Cottrell precipitator.³ In 1938 there were produced in the United States 24,983 tons of white arsenic, of various grades, the crude priced at \$21.80 and the refined at \$29.30 a ton; 1,000 tons were imported besides 9929 tons, of which 76 per cent came from China.

The imports in 1939 were 14,674 tons. The consumption is due partly (87 per cent) to the manufacture of arsenical insecticides, to a lesser extent to the manufacture of plate glass (3 per cent). Because of the rapid growth in the use of lead and calcium arsenates, the yearly consumption of white arsenic will undoubtedly increase. At the present time, it is well to remember that white arsenic plays a part in chemical warfare. White arsenic heated with Chile saltpeter gives sodium arsenate, Na_2AsO_4 , and this in solution may be used to make the lead and calcium arsenates. Other ways to change the white arsenic, As_2O_3 , to arsenic acid, H_3AsO_4 , are by means of chlorine in presence of water,⁴ followed by sufficient concentration to drive off the hydrochloric acid formed in the reaction, or by heating with nitric acid and evaporating to a syrup. Lead arsenate may be prepared by suspending litharge, PbO , in a solution of arsenic acid in the presence of nitric acid or acetic acid⁵; an improvement is to use sublimed lead oxide (yellow) (PbO) made into a cream with water, and add to this solution of arsenic acid.⁶ The reaction takes place at room temperature; the lead arsenate precipitates and is filter-pressed and sold as a paste, or, as is the general custom, is dried and shipped as a powder.

The precipitate does not settle very well; indeed it is essential that it remain in suspension for long periods when made up for spraying; a common way was made to avoid any kind of washing by adding magnesium hydroxide, $Mg(OH)_2$, after the lead oxide had reacted, to bind the remaining arsenic acid or arsenate of sodium.⁷ The resulting product is a mixture of sodium and lead arsenates, $MgHAsO_4$ and $PbHAsO_4$, which is said to be an excellent insecticide.

An excess of lead is always provided, for soluble arsenic beyond a certain limit (1 per cent As_2O_3) is prohibited by the Federal Insecticide Act of 1921.

Footnote 43.

Tariff Information Survey, FL6, U. S. Tariff Commission, Washington, D. C., 1921, p. 11.

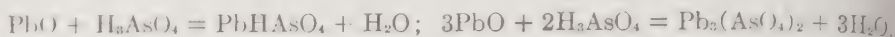
Patent 1,169,114.

Patent 892,603.

Patent 1,228,516.

Patent 1,417,232.

1910. When lead nitrate is treated with arsenic acid, the acid lead arsenate, PbHAsO_4 , precipitates and remains in suspension even better than a neutral salt, contains more arsenic, and is quicker in action on the insects. When lead acetate is used instead of the nitrate, the neutral lead arsenate, $\text{Pb}_3(\text{AsO}_4)_2$, is formed; this is less injurious to foliage, and remains in suspension very well; it is used for peach and plum trees. In the process of making lead oxide, the kind of lead arsenate formed is determined by the amount of lead oxide used to a given amount of arsenic acid. Both the acid and neutral lead arsenates are insoluble in water.



Lead arsenate may also be manufactured in the dry way, by burning powdered lead sulfide or metallic lead and white arsenic in a blast of hydrocarbon fuel; the oxidation and combination occur in the high heat of the burning fuel. The lead arsenate formed is collected in settling chambers and bag filters.⁸

Calcium arsenate, also a white powder or paste, is made by running a solution of calcium chloride, CaCl_2 , into an alkaline solution of sodium arsenate, Na_2HAsO_4 :



the hydrochloric acid is removed by the alkali in the sodium arsenate solution. The calcium arsenate is insoluble; it precipitates and is filter-pressed and shipped as a paste or dried to a powder.

Calcium arsenate may be substituted for lead arsenate, except in treating trees with tender foliage; it is more injurious than the lead arsenate; it is less adhesive, but this may be remedied by using it in conjunction with Bordeaux mixture, or with lime. The great advantage of calcium arsenate is its low price,⁹ which has permitted among other things its use in cotton fields for the destruction of the dreaded boll weevil. Calcium arsenate has been found a superior insecticide for this pest, and the general method of application is as a dust, without dilution.¹⁰ There were produced in the United States in 1939, 59,568,596 pounds of lead arsenate and 39,281,758 pounds of calcium arsenate.

Even at 6.75 cents, calcium arsenate is too dear for general use in cotton fields against the boll weevil. Dilution would not do, but a method of preparation has been found by means of which an inert kernel of calcium carbonate is coated with calcium arsenate, the resulting powder being as effective as pure calcium arsenate. This important contribution is from the Chemical Warfare Service Boll Weevil Investigation Board, and is an example of the peace-time functions of this bureau. Mixtures of precipitated chalk and white arsenic are heated with excess air at 650°

⁸ U. S. Patent 1,175,565.

⁹ Calcium arsenate 6.75c; lead arsenate 11.5c; Paris green 22c (1937).

¹⁰ "The principles of insect control." Wardle and Buckle, Manchester, University Press, 1933. The cotton fields are dusted from airplanes as well as by means of tractor or motor-driven sprayers. A service in Stuttgart, Arkansas, for example, operates 18 planes (called ships), taking contracts where in the United States. There is claimed for the airplane distribution method a greater speed besides rapidity; 300 to 400 acres per hour are dusted, whereas with the ground methods, 50 acres a day is the average man's work. The ship flies 3 feet above the top of the plants; if necessary closer, such as 6 inches (wind). This is exceedingly dangerous work for the plane operator.

one is changed to the pentavalent form, as normal tricalcium arsenate. It has been established that this material, with only 24 per cent As_2O_5 , is effective against the boll weevil as ordinary calcium arsenate, with 40 per cent As_2O_5 .



FIGURE 204.—The full-size sprayer assembly consists of a tractor, and the spray tank with a small pump for the liquid and a blower. Pump and blower are operated by a separate gasoline engine. Dry dust is applied with very similar apparatus. (Apple orchard, Cobblestone Fruit Farm, Sodus, N. Y.)



FIGURE 205.—The lime-sulfur solution is atomized in the nozzle and the rich mist directed into the tree. Pump for the liquid is at left; the blower is just behind the operator. (Spraying McIntosh apple trees, Sodus, N. Y.)

In spray form, the proportions recommended for both lead arsenate and calcium arsenate are 1 pound of the powder to 50 gallons of water (about 2 per cent). The method of spraying trees in orchards requires two men: a gasoline-driven pump and a tank are placed on a flat-topped wagon. One man guides the horses or the tractor, the other directs the spray. Paris green is used in appreciable quantities, though smaller than those of the preceding two arsenicals. Many farmers consider paris green the best against the potato bug. The method of manufacture is to add a solution of copper acetate to a solution of arsenious acid, H_3AsO_3 ; there is formed a copper acetoarsenite of indefinite composition. This is filtered and dried. Paris green has a higher tolerance for water-soluble materials than lead arsenate; it must not exceed $3\frac{1}{2}$ per cent As_2O_3 . The production in 1939 was 2,040,307 pounds.

Hellebore is the powdered root of the hellebore plant, *veratrum album*; it contains alkaloids which poison the insect but, in the small quantities used, do not affect man. When applied dry, the powder is diluted by mixing with flour or lime; when applied wet, the dilution by the water used is sufficient. Hellebore serves mainly for restricted areas, such as gardens and lawns.¹¹

Silicates have been introduced as insecticides; see Chapter 3 for their manufacture, and "The use of silicates as insecticides," S. Marcovitch, *Ind. Eng. Chem.*, 18, 572 (1926).

The Contact Insecticides. The contact insecticides are effective against the boring insects which have soft bodies, such as scale insects, plant pear thrip, red bug, red spider, and others. By means of these chemicals the insects are poisoned, paralyzed, or, killed by covering the skin with a film of oil which closes the breathing pores. Lime-sulfur, nicotine, solutions, kerosene, and oil emulsions are the important members of this group.

Lime-sulfur is used both in solution, as a spray, and in the dry powder form, as a dust. It is manufactured by boiling sulfur in milk of lime, with the formation of calcium polysulfide and small amounts of a number of sulfur compounds of no importance. The solution is yellowish-brown; after filter-pressing or decanting the clear liquor, it is concentrated to 32° F. cold, when it contains about 24 per cent of sulfur in solution. This solution is shipped in tight oak barrels, and is diluted with 8 parts of water for the San José scale, 16 parts for the peach leaf curl, 42 parts for apple tree spray, and 54 parts for pear and cherry trees.¹² There is also in wide use a home-made lime-sulfur solution, which has the same composition and effectiveness as the commercial material. Lime-sulfur is also sold in dry form, which may be applied as a dust. The reported production of lime-sulfur solution was 9,491,068 gallons, at 9.7 cents a gallon (1933).

Nicotine in the form of nicotine sulfate is made from refuse tobacco and is sold as a 40 per cent solution. This is diluted so that the spraying liquid contains not less than 0.06 per cent nicotine; it is advisable to dilute in a soap solution, which acts as a spreader, containing 2 pounds of soap to 10 gallons of water. A satisfactory nicotine extract may also be home-made by steeping stems and sweepings of dried tobacco in water at ordinary temperature. If refuse tobacco is purchased, the cost is reduced, as the extracted material is a good fertilizer. The strength of the extract is fixed by using definite weights of tobacco, and consulting the table furnished by the United States Department of Agriculture.¹³ Such home-made extracts contain the nicotine in the form of the free base; the commercial, concentrated extract is the sulfate of nicotine, because the free base is volatile and would be lost during concentration, whereas the sulfate is fixed.

Nicotine powder is made by pulverizing stems, and may contain very little nicotine. The strong extract may be applied in the form of a dust by mixing it with gypsum, kaolin, or hydrated lime, or a mixture of these; the choice of the added solid has a definite influence upon the effectiveness of the dust.

Soap solutions are usually fish-oil soaps, containing 1 pound of soap to 10 gallons of water or more; the strength depends on the kind of insect to be destroyed. Fish-oil solutions are efficient against plant lice. The soap solution is frequently used with nicotine solutions, arsenate of lead, or Bordeaux mixture. The soap may be purchased, and may be a potassium or sodium soap, preferably the former; it may be home-made from fish-oil and lye; in either case, the soap retains a strong fish-like odor.¹⁴

¹² "Injurious Insect Pests and Fungous Diseases," reference 1, p. 59.

¹³ U. S. Dept. Agr., *Farmers' Bull.* No. 908, 41 (1920).

¹⁴ U. S. Dept. Agr., *Farmers' Bull.* No. 908, 36 (1920).

kerosene, crude-oil, and lately lubricating-oil emulsions have been used with success. A kerosene-oil emulsion may be made as follows: one-half pound of fish-oil soap is dissolved in 1 gallon of water, and 2 gallons of kerosene added to the hot solution; by pumping it back and forth, or by mechanical agitation, a creamy emulsion forms, which does not separate on cooling. For use on dormant trees, the dilution is 1 part to 7 of water.¹⁵ Other emulsions are made in a similar way.

Miscible oil emulsions are made by mixing an emulsifying solution containing fish-oil soap, carbolic acid and kerosene, with the "miscible oils," in oil (28° Bé.) and rosin oil.¹⁶

Pyrethrum and rotenone, either in powder or as the extract, are widely used as horticultural and household insecticides.

Insecticides in Vapor and Gas Form. Stored wheat and other grains are infested by insect pests which are readily destroyed by pouring carbon disulfide on the grain and closing all outlets; such fumigations are practiced only when the material is contained in a building which can be closed hermetically during treatment. Carbon disulfide and air mixtures are dangerous; to avoid this danger, a new fumigant has been developed, a mixture of ethyl acetate and carbon tetrachloride which is non-explosive, vaporizes almost as readily, and is nearly as efficient.

Hydrocyanic acid, HCN, is an excellent fumigant, and although a deadly poison to man, may be handled safely. A dish containing the proper amount of sodium cyanide is placed underneath a bottle containing sulfuric acid, and can be upset from near the door by an arrangement of strings and pulleys. As the operator is about to step out, he pulls the string and opens the door. This gas is applied to citrus trees in California, by placing under the tree a cotton duck bag which reaches to the ground; the gas is generated by acid on sodium cyanide and destroys the insects without hurting the tree. Calcium cyanide is also used.

"Fumoxide" is the trade name for a mixture of 1 part ethylene oxide and 3 parts carbon dioxide, a safe and effective fumigant; it is non-flammable and non-explosive. It is obtainable compressed to a liquid in steel cylinder; the material issues from the cylinder in a fine spray or mist which vaporizes immediately.

The peach borer works near the ground and cannot be reached by sprays; para-dichlorobenzene, a solid, placed in a small trench around the base of the tree, destroys it.

FUNGICIDES

Fungous diseases which attack the fruit-trees, vines, and farm crops are perhaps more serious even than the insect pests, because once the fungus has grown, it is so tough that it resists chemicals; it is only when the spores are young and tender that they can be destroyed with chemicals. The work against fungous diseases thus takes on the aspect of prevention rather than cure; in keeping with this policy, nursery stocks and seedlings are fumigated¹⁷ and dipped before sale.

¹⁵ *Injurious Insect Pests, etc.*, reference 1, p. 55.

¹⁶ *S. Dept. Agr., Farmers' Bull. No. 908, 32 (1920).*

¹⁷ *For example, the dust Seneslan (Dupont) containing 35 per cent hydroxymercuriphenol, applied to seedlings, destroys fungi (which include molds and bacteria).*

Some of the fungous diseases are mildews, apple and other scabs, leaf spot, brown rot of plum and peach, and bark cankers. The important fungicides are sulfur, Bordeaux mixture, lime-sulfur, already listed as contact insecticide, formaldehyde, corrosive sublimate (HgCl_2), and a number of organo-mercuric compounds.

Sulfur, in the form of a fine powder under the names of dusting sulfur (99 per cent S), sulfo-dust, dry mix (61 per cent S) and others; is applied mainly as a dust, in a few cases as a suspension in water or better, soap solution. It is estimated that in Europe over 100,000 tons of powdered sulfur or flowers of sulfur (sublimed) are used every year against the microscopical fungus *oidium*, which causes the grape vine leaf to dry.

The main sources of sulfur are Sicily and the Louisiana and Texas deposits; sulfur occurs in many other places, however, such as Japan, Mexico and in the state of Wyoming. In Sicily, the sulfur occurs mixed with iron ore and gypsum; it is purified by heating and draining or running off the heavy sulfur; the fuel is sulfur. In the coastal plain of the Gulf of Mexico, a strip of land 225 miles wide is sulfur-bearing; it lies partly in Louisiana, and partly in Texas. The sulfur lies at depths of 600 to 1100 feet, and the deposits average 125 feet. It is lifted to the surface from deposits between 600 and 2000 feet deep by means of the Frasch process.¹⁸ The sulfur pocket must be covered by a fairly thick and tight cap, for the superheated water must be kept under 100 pounds gauge pressure, in order to retain for it a temperature of 340° F. (171° C.). The heated water is forced down 6-in. casings into the deposit; the melted sulfur [melting point 112.8° C. (235° F.)] is forced upward through a 3-inch casing strung inside the outer 6-in. one. A 1-inch pipe inside the 3-inch one carries compressed air (500 pounds) to the liquefied sulfur and, mixing with it, divides it into gulleys separated by the air, which makes a column easier to lift. Not only must sulfur be located, but other conditions must be met before the mining of a given deposit can become a reality. For the production of 1000 tons per day, 2-3 million gallons of water are required, a 4000-horsepower boiler plant, five pipe lines and bins for receiving the liquid sulfur, and the possible necessity of disposing of "bleed" water from non-producing wells in the same dome. Continuous operation in the Frasch process is essential, for, if interrupted the liquefied sulfur in the formation congeals and "freezes" the pipes in each hole.

TABLE 90.—Sulfur production and uses in the United States in long tons.*

	1939	1940	1941
Sulfur mines	2,090,979	2,732,088	3,150,000
Non-acid uses of sulfur	495,000	610,000	705,000

* *Chem. Met. Eng.*, 49, 83 (1942).

The main uses of sulfur are as a fungicide, for making lime-sulfur, in the sulfite pulp process in paper-making, for manufacturing sulfuric acid (supplementing pyrite), for vulcanizing rubber, and for the manufacture of carbon disulfide.

¹⁸ "The manufacture of sulfuric acid in the United States." Wells and Fogg, *Dept. Interior* No. 184, p. 27; see also *Ind. Eng. Chem.*, 4, 136, 140, 143 (1912)

¹⁹ J. H. Pollard, *Chem. Met. Eng.*, 39, 394 (1932).

the production of sulfur as brimstone in the United States, mainly from Texas and Louisiana, is shown in Table 90. By-product sulfur is presented in Chapter 14.

Bordeaux mixture is probably the most important fungicide used in the United States; it may be purchased in the form of a powder and made up in water, or it may be home-made. It consists of copper sulfate and lime. For the home-made spray, ready to apply to the crops, the proportions are as follows: 4 pounds of copper sulfate $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$, called bluestone, dissolved in 25 gallons of water; 4 pounds of fresh stone lime, or quicklime (CaO), are dissolved in 25 gallons of water, and the two solutions are



FIGURE 206.—Melted sulfur brought to the surface from the subterranean deposit and being discharged into a sulfur vat, at New Gulf, Texas. The discharge pieces are the latest type; they spread the flow which formerly was concentrated in a stream. (Courtesy of the Texas Gulf Sulfur Company, New York, N. Y.)

in the spray tank itself, for example. The concentration is correct for spraying; a little less bluestone is taken for spring spraying. This gives a bluish deposit, which is very noticeable on the green leaves.²¹ Formaldehyde solutions are used to prevent potato scab, oat smut, the rust smut of wheat, and onion smut. The method for potatoes is to treat the seed potatoes in a solution containing 1 pint of 40 per cent formaldehyde solution (CHOH) in 30 gallons of water, for two hours. The oats are spread on the floor and the solution poured on them. Other uses of formaldehyde will be found in Chapter 35.

Mixed Sprays and Mixed Dusts. It is often desirable to apply two or even three at the same time, in order to save labor; an insecticide and a fungicide may be mixed, since insects and fungous disease often come together. Mixed sprays are widely used; thus lime-sulfur, arsenate

²¹ U. S. Dept. Agr., *Farmers' Bull.* No. 908, 39 (1920).

The discovery of the fungicidal value of Bordeaux mixture was accidental; while walking in a vineyard the French scientist Millardet noticed that the vines at the edge of the vineyard had not lost their leaves while the rest had; the custom was to spray the edges with a mixture of copper sulfate and lime in order to scare off thieves who mistook the bluish deposit for poison (1882). This led to experiments by Millardet and Gavon, which established the value of the same mixture as a fungicide.

[illegible]

FIGURE 207.—Chemicals which may be used mixed together, so as to allow treatment for two or more diseases. Only the chemicals within heavy lines may be mixed. (From U. S. Dept. Agr., *Farmers' Bull.* No. 908.)

DISINFECTANTS

The chemical industries perform an important service in furnishing disinfectants which supplement sterilization by steam or flame. The function of a disinfectant is to kill bacteria and to prevent further growth of new cul-

²² U. S. Dept. Agr., *Farmers' Bull. No. 908*, 73 (1920). "The principles of insect control" West and Buckle, p. 118. See reading references. A highly esteemed farm journal is the *Rural New Yorker* published at 333 West 30th Street, New York.

A germicide also kills bacteria, but its power to prevent further growth is secondary; an antiseptic inhibits bacterial growth without necessarily killing.

Among the important chemical disinfectants are: phenol, cresol, guaiacol, formaldehyde, potassium permanganate, bleaching powder, calcium hypochlorite, sodium hypochlorite, chlorine, bichloride of mercury, aristol, hydrogen peroxide, and mercurial phenols. The standard is a 5 per cent solution; the power of other substances is expressed in terms of the standard, and this value is known as the phenol coefficient. The method is to make a bacterial count before and after application. The phenol numbers vary with different bacteria.

Carrel-Dakin solution,²³ discovered during the war of 1914-18, is now classed as an antiseptic; it consists of a 0.5 per cent sodium hypochlorite solution, made from bleaching powder, very slightly alkaline. It is used to irrigate wounds, so that the dead tissue is dissolved, thereby destroying the food of bacteria, which die as a consequence.

Sodium carbonate is a rat poison, harmless to dogs. A 1000 water solution of hexylresorcinol (*n*-hexyl-2,4-dihydroxyphenol) kills bacteria in 15 seconds; it has a low surface tension, which permits penetration into small spaces, an important advantage. It is non-toxic.

WOOD PRESERVATION

The preservation of wood for railroad ties, fence posts, and in general of wood used outdoors is an important problem. In the past, treating with creosote oil (*see* Chapter 14) has been the chief method, and remains an important one. The practice is to heat the wood in order to drive out moisture, then apply a vacuum to the containing chamber in order to free the pores of the wood, and send in hot creosote, under gradually rising pressure. In 1940, there were produced in the United States 119,678,785 gallons of creosote oil, a coal distillate, valued at 12.1 cents a gallon. Essentially all is used for wood treatment.

Another chemical agent used for preserving lumber is zinc chloride; 100 million pounds are used for this purpose in a normal year. The preservation of wood for marine purposes is a specially vital problem. In infected areas, the shipworm causes untold damage in a short time. *Teredos* and the *Bankia gouldi* are the two best-studied examples of shipworms. They bore into the wood of piling or ship-bottom and in time honeycomb it with burrows so that the wood collapses. The following investigation²⁴ conducted by the Chemical Warfare Service was in a preliminary way that certain of the war gases, best disinfectants, would be superior agents for marine preservation.

OTHER PATENTS

Patent 2,064,728 and 2,060,311, making colloidal sulfur; 2,044,214, sulfur refining process; 2,046,546-7-8, process for removal of insecticidal residues from fruits and vegetables; 1,928,968, colloidal dispersions of rotenone by the aid of tannic acid; 1,875,466, preparation of arsenical compounds suitable for use as insecticides; 1,875,466,

²³ Pharmacopoeia, 10th ed. (1928).

²⁴ Am. Railway Eng. Assoc., 28, No. 290 (1926).

esters of the fatty acids derived from animal or vegetable fats or oils are insecticidal and non-injurious to plant life; 1,877,851, an insecticidal containing petroleum, a compound of nicotine with an oil-soluble sulfonic acid derived from petroleum, an emulsifying agent; 1,842,443 and 1,863,519, an insecticide containing aluminum sulfate, potassium hydroxide, and hydrofluoric acid; 1,849,778, a fungicidal dust composition containing a complex copper salt of mercury thiocyanic acid; 1,890,777, a dust disinfectant, from mercuric chloride, chlorophenol, sodium carbonate, hydrated lime; 1,801,114, disinfectant using 500 parts hydrated lime, 200 parts water, 50 parts mercury acetate; 1,791,430, a fungicide and bactericide consisting of calcium sulfate and lime; U. S. Patent 2,279,879, on mixing powdered carob beans with arsenate insecticide to nullify its poisonous effect on humans.

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the place which natural rubber holds in our economic life has been under-
 by the loss of importations from the Far East, and by the occupation
 of Java and Java by the Japanese. Natural rubber had become an all-
 se servant; it has served us well in the form of the vulcanized, long-
 elastew; and it has been made to serve in many ways for which it is
 art icularly suitable, when in our haste we could not stop to develop
 al product. Perhaps now that our stocks are running low, we shall
 to develop many new products each one of which will take over one
 hundreds of duties we have assigned to the versatile substance, rub-
 The remedy for the shortage of india-rubber lies not in developing a
 all-purpose substitute, but in producing a multiplicity of new sub-
 s, each of which will perform one duty, and only one, supremely well.
 g for the new all-purpose synthetic rubber only those duties which
 ly belong to it.

Without the development of good synthetic rubbers, Germany could not
 embarked on World War II; the rapid expansion of this industry in
 ntry is vital both to the conduct of the war, and to the maintenance
 customary way of life.

Chapter 39

Rubber*

The hydrocarbon, rubber, $(C_5H_8)_x$, is found in many plants, trees and
 . Over 98 per cent of the world's supply, however, comes from the
 tree, *Hevea brasiliensis*, and 97 per cent from cultivated plantations
 s tree, mostly in Ceylon, British Malaya and the Dutch East Indies.
 sources such as goldenrod, milkweed, etc., are difficult to utilize com-
 ally on account of the large amounts of resins and other substances
 ated with the rubber. Only the guayule shrub, native to Mexico and
 uthern part of the United States and now grown commercially in Cali-
 promises a commercial supply at reasonable cost. When cultivated,
 rub at four years of age is pulled up bodily, and yields some 17 per
 bber on the weight of the plant.

In a primitive form, rubber has been known in America for centuries;
 logical records in Honduras dating back to the 11th century show the
 solid rubber balls in native games, and early Spanish explorers men-
 the use of rubber latex to coat cloth and render it waterproof. In
 e, the house of James Lyne Hancock, Ltd., London, was established
 O, and claims to be the oldest rubber factory in the world. Modern
 products, however, did not begin to appear until 1839 when vulcaniza-
 the reaction of sulfur with rubber to produce a chemical and physical
 e, was discovered by Charles Goodyear, and a factory started at
 field, Massachusetts, in 1841. By 1876, the manufacture of rain-
 close collaboration with Mr. Raymond B. Stringfield, Consulting Chemical Engineer, Los
 California.

credit for the discovery of vulcanization should be granted to four individuals, in equal
 Dr. F. W. Luedersdorff (1832), Nathaniel Hayward [U. S. Patent 1090, (1839)], both of whom
 d the beneficial action of sulfur, Charles Goodyear [U. S. Patent 3633, (1841)], and Thomas
 (in England), both of whom discovered the importance of heat in sulfur vulcanization. [From
 erbilt (1936) Rubber Handbook, p. 111.]

coats, carriage tires and other rubber articles was a thriving little business. Rubber coming from the Amazon region in Brazil, where it was gathered by natives from wild trees in the tropical forests. Henry Wickham, British explorer, envisioned the future growth of the industry and the necessary cultivated plantations of rubber trees to assure a steady source of supply. He determined to make the industry independent of the Brazilian monopoly, and succeeded in gathering 70,000 seeds of the *Hevea brasiliensis* in Brazil and transporting them to England. The seeds were raised at the Kew Gardens in London, only 4 per cent reaching the plant stage; the seedling trees obtained were transplanted in Ceylon. From this start has come the rubber industry, to supply which, plantations in 1940 covered over 8,000,000 acres and produced 1,391,834 long tons of rubber. The best buyer was the United States, with imports of 811,564 long tons in 1940, much of which went into war uses.

The rubber-producing countries of the world, in the order of their 1940 production, are as follows: British Malaya, 540,417 long tons; Netherlands East Indies, 536,740; Ceylon, 88,894; Indo-China, 64,437; Thailand, 43,940; Sarawak, 35,166; India and Burma, 23,317; North Borneo, 17,623; South America, 17,601; Africa (except Liberia), 10,103; Liberia, 7223; Mexico (guayule) 4106; Oceania, 2267.

Plantations. The best practice in Malaya provides 100-120 trees per acre, to yield an average of 425 pounds of dry rubber per acre per year. The trees begin to yield latex when they are six years old, and continue to yield over forty. The size of the full-grown rubber tree is about that of the maple. In the *Hevea brasiliensis*, rubber occurs as a milky latex in a series of vessels just under the bark. Native tappers remove a shaving of bark from a diagonal cut extending one-third around the tree, and collect in small cups the latex which flows out. Trees are most economically tapped every other day, yielding about an ounce of latex. The latex, which averages about 35 per cent rubber in the form of particles 1 to 2 μ in diameter dispersed in a watery serum, is brought to a collecting station, diluted to about 15 per cent rubber content, and coagulated by addition of acetic or formic acid.²

The bulk of the rubber comes on the market as *ribbed smoked sheet*. This is made by sheeting the coagulated rubber on even-speed rolls with light washing, and drying from 7 to 11 days at 40 to 50° C. (104-122° F. in an atmosphere of smoke from burning fresh wood.³ The smoke turns the rubber brown, and acts as a preservative, preventing the development of mold in the serum substances remaining in the rubber. The smoked sheets are pressed into square bales of 200 to 220 pounds, and protected with plywood for shipment.

Another important grade of rubber is *pale crêpe*. For this, sodium bisulfite is added to the latex before coagulation, and the coagulum washed thoroughly on differential-speed rolls to tear the rubber apart and remove

² The rubber latex particles exhibit a lively Brownian movement under the ultra-microscope. The particles are spherical in the latex from young trees, slightly egg-shaped if from older trees. One feature is that the particle carries a drop of hydrocarbon oil contained in a sack made of the same oil and gelatinized, and the whole stabilized on its surface by a protein layer.

³ The name of the plantation is embossed in the sheet.

substances. The sheets are then dried without smoking, yielding a fish-white rubber which is baled as before. Other lower grades, such as brown crêpe, blanket crêpe, rolled brown, and plain unsmoked sheets are produced by various plantations.

Fluctuations in supply and demand, coupled with arbitrary economic restrictions, have caused the price of rubber to fluctuate between a high of 25 cents per pound in 1925 and a low of 2½ cents per pound in 1932. Plantation operations have been greatly improved, and where in 1920 plantation rubber was approximately \$0.21 per pound, it is now estimated that, except for government's interference, rubber could have been landed in New York from the plantations to sell profitably at \$0.07 per pound.

Vulcanization. Raw rubber has few commercial uses as it softens when heated, stiffens when cooled, is soluble in coal-tar or petroleum solvents, is sticky, and has low tensile strength and other unsatisfactory physical properties. By mixing with sulfur, in the form of ground sulfur (through a mill), usually not over 3 per cent on the rubber, and heating, a process called vulcanization takes place; part of the sulfur combines chemically with the rubber hydrocarbon, and changes its physical properties so that it is no longer affected by ordinary temperature changes, is swelled but not dissolved by solvents, and has greatly increased strength, abrasion resistance, etc. Vulcanization may be carried out in various ways: in hot water or air (as with rubber gloves), in an autoclave with steam (as with rubberized fabric), or in molds heated with steam (as with tires) and pressed by the platens of a hydraulic press (as with heels and most other rubber articles).

Vulcanization is a progressive reaction; it should be allowed to progress to a definite point, and not beyond. Rubber which has not been heated long enough is said to be "undercured," while rubber which has been heated too long is "overcured."

When sulfur and rubber alone, approximately 120 min. at 287° F. (141.7° C.) are required to accomplish vulcanization. About 1914, organic accelerators were introduced which greatly speed up this process. A few inorganic compounds like litharge, lime and magnesium oxide have accelerating action, but have been almost entirely replaced by more powerful organic compounds. The latter are used in amounts varying from 0.1 to 1.5 per cent, and certain combinations can reduce the time of "cure" or vulcanization to as little as 3 min. at 200° F. (93.3° C.). Commonly used as accelerators are captobenzothiazole (Captax), $C_6H_4.N:C(S)SH$; diphenylguanidine (DPG), $(C_6H_5NH)_2C:NH$; tetramethylthiuramdisulfide (Tuads), $(CH_3)_2NCS.S.CSN(CH_3)_2$; and zinc dimethyldithiocarbamate (Zim), $(CH_3)_2NCS.S]_2Zn$.

Uncured rubber deteriorates from oxidation, particularly if exposed to sunlight. Chemicals which retard this deterioration have been developed and are widely used. These are usually called *antioxidants*, and 1 per cent is sufficient to increase greatly the life of the rubber product. Commonly used antioxidants are aldolalphanaphthylamine and phenyl betanaphthylamine.

Compounding, compounding ingredients, and reasons for their selection. The whole art of mixing other ingredients with rubber and of processing the

mixed compound to control its physical properties, both before and after vulcanization, is called *compounding*. The use of *sulfur*, *accelerators*, *antioxidants* has already been mentioned. Other materials are used as *accelerator activators*, *accelerator retarders*, *rubber substitutes*, *softeners*, *stiffeners*, *odorants*, *fillers*⁴ and *pigments*.

Almost every rubber compound carries from 1 to 5 per cent zinc oxide and at least 1 per cent stearic acid or suitable substitute, their purpose being to activate the accelerator present and enable it to produce its full effect. Occasionally materials such as salicylic acid are added to retard the effect of the accelerator, particularly at low temperatures, so the compound will not cure prematurely during processing.

Rubber-like products called *factice* can be made by reaction of sulfur or sulfur chloride with vegetable oils, and find use in some soft rubber products such as erasers. Certain blown asphalts, known as *mineral rubber*, may be substituted for part of the rubber in stocks such as wire insulation where they aid the flow of the compound as it is extruded, and also act as a general diluent in inexpensive stocks.

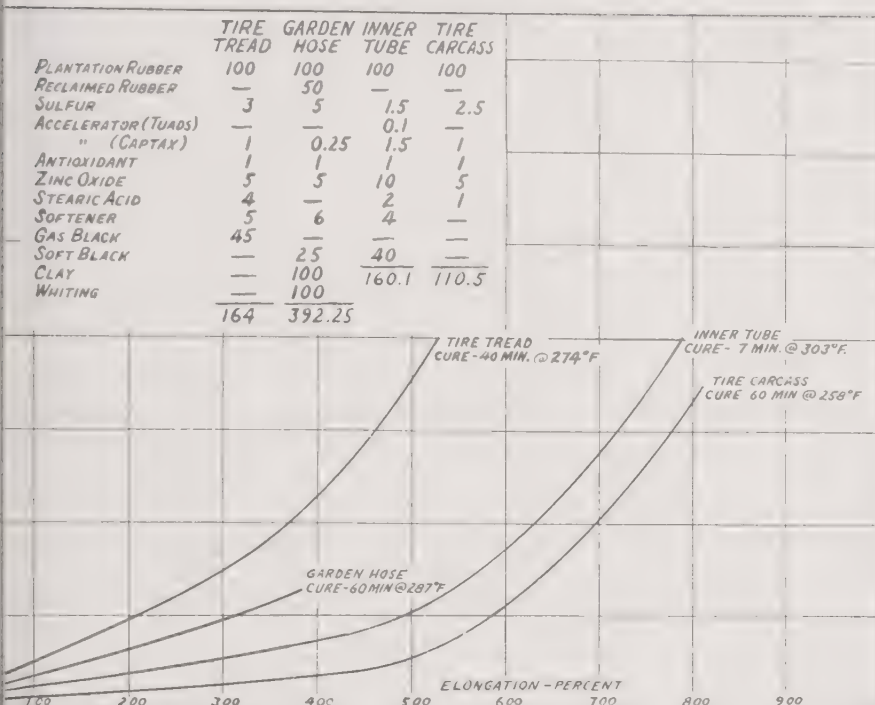
The mixing of the compounding materials is generally done on mixing rolls, the various materials being added one by one in the selected order. Raw rubber is tough, and requires mastication on a mill until it is hot and plastic before compounding ingredients can be added, and the compound sheeted or shaped for the next operation. Softeners such as vegetable and mineral oils, waxes, tars, pitches and resins are added to save time and power and facilitate handling. Occasionally, particularly with highly compounded stocks, stiffening is desirable in the uncured compound, and this can be accomplished by the addition of small amounts of benzidine or *p*-aminophenol. For some household purposes the odor of rubber is undesirable, and odorants have been developed that, in quantities as low as .25 per cent, persist through vulcanization and aid the sale of the product.

As "pure gum" products, that is, pure vulcanized rubber products, are too soft and elastic for most commercial uses, reinforcing agents are commonly added to the rubber; they increase the hardness, stiffness, tensile strength, and resistance to cutting, tearing and abrasion. Their action is purely physical, and is due chiefly to their fine particle size and good dispersion in the rubber. The most important reinforcing agent is carbon black made by the channel process; it is used in all articles which receive extremely rough service, such as tire treads, and conveyor belts. Zinc oxide is used when the stock must be light-colored; it is not as effective as carbon black, and is much more expensive on a volume basis. Many non-reinforcing fillers, such as whiting, clay, or slate flour, may be used in certain places to add weight, stiffness, reduce elongation, improve processing or reduce costs. Such uses are entirely legitimate, there being no object, for instance, in having high abrasion resistance in a product not subjected to rough usage. Color pigments, dyes or lakes may be used where colored products are desired.

⁴ For comparison purposes, it is customary to calculate all formulae for rubber compounds in per cent by weight on the weight of the rubber present, or in volumes of filler per 100 volumes of rubber. The latter is particularly useful as it takes into account the specific gravity of the materials used. The rubber has a sp. gr. of .92, ZnO 5.57, and carbon black 1.80, and either 55.7 lbs. ZnO or 18.0 lbs. C would be a 10 vol. loading when mixed with 92 lbs. rubber.

compounding formulae for four typical rubber stocks, tire tread, hose, inner tube, and tire carcass are given, with a set of stress-strain curves for these same stocks after vulcanizing at the temperature and period given on the graph, Figure 208. In a vulcanized article, the combined sulfur to the rubber is called the *vulcanization coefficient*. Of great value is also the ratio of accelerator to rubber.

Stock Preparation. The main operations in preparing rubber stock are *calendering* and *extruding* or "tubing."⁵ The rubber compound



208.—A set of stress-strain curves of typical rubber stocks; above are the four formulae for the compounding, all based on 100 parts of gum rubber or plantation rubber (crêpe or smoked sheets). [From the practice of Mr. Stringfield.] The reader will please note also the temperature and time of curing.

used for two purposes; first, to mix and thoroughly disperse the ingredients, and secondly, to plasticize the rubber and render it more adaptable for operations. This is done on two types of equipment, mixing rolls or Banbury mixers. For large production, mixing rolls are 84 inches long and 22 or 26 inches in diameter, and of cast steel 5 inches thick, the inner surface being cooled with a spray of water. Such rolls are mounted together horizontally, geared to revolve toward each other at a ratio of about 1.0:1.25 and a surface speed on the slow roll of 100 feet per minute. Rubber placed on the rolls is squeezed downward by the "bite," and allowed to sheet around the slow roll back into the nip. It was formerly necessary to wash and dry the raw rubber to remove sand, bark, etc., but plantation rubber is now so clean that this operation is usually omitted. For some special purposes, as for tires, rubber may be strained by extruding through a fine screen.

excess or "bank" on top of the rolls. One roll is adjustable to vary thickness of the sheet between $\frac{1}{4}$ and $1\frac{1}{4}$ inch. When the rubber is enough, the operator begins adding the other ingredients in proper "working" the batch from time to time, by cutting the sheet on the to bring fresh material through the "bite." A batch may vary from 350 lb. depending on its type, and may require from 10 to 60 minutes milling. Approximately 100 h.p. are required for operation, most of which appears as heat in the rubber stock, which has to be rapidly removed by cooling water to prevent premature vulcanization, or "scorching." Even with this cooling, the stock is usually about 200° F. (93.3° C.), and when mixing is completed, is cut off in slabs about 3 feet square and dipped in slurry of tale and water to cool and prevent sticking together. Small mills are used for sheeting out stock from Banbury mixers, and for "warming up" stock for calenders and tubers.

The Banbury mixer is an enclosed machine with two water-cooled rotating rotors operating in a water-cooled chamber. Mixing is very rapid, for example: an 84-inch mill will mix a 350-pound batch of tread stock in 30 minutes, while a number 11 Banbury will handle 650 pounds of the same stock in 18 minutes, or 3.11 times faster. The Banbury stock will require an 84-inch mill to sheet out and batch off the mixed stock.*

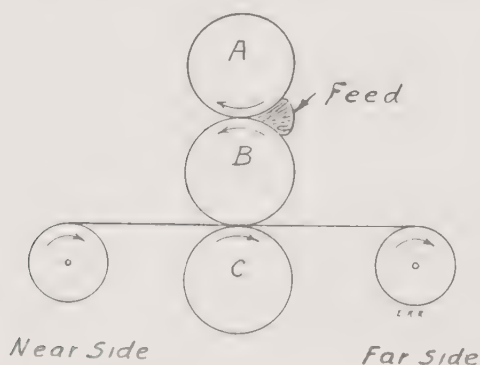


FIGURE 209.—Diagram of a calender as used for applying a rubber coat to fabric.

the use of suitable compounds, mixing in a Banbury mixer results in a large saving of power. Several sizes are available, taking batches up to 650 pounds.

Calenders are usually 3-roll machines (Fig. 208) and are used for three general types of work, *frictioning*, *skim-coating* and *sheeting*. Cotton fabric is "frictioned" by passing it over roll C with roll B running at a high speed, resulting in wiping the rubber compound into the voids in the fabric. Skimcoating is a similar operation, but with roll B at the same speed as C so that a film of rubber is pressed into the fabric. For sheeting, roll C is lowered and a cotton "liner" used, the sheet of rubber formed between A and B being led into the liner in which it is wrapped. By placing rotating knives against the near side of B, strips may be cut of any desired width.

* Generally speaking, a Banbury-mixed stock is usually somewhat tougher than the same stock mixed on a mill, and this gave originally a great deal of trouble, but modern compounding with the use of softeners has overcome the difficulty, and the practice of sending the stock to the tubers and calenders without allowing it to cool has effected large savings.

lled up in the liner passing over C, the excess rubber between the returning to the feed.

The extruding machine or "tuber" is essentially a steel cylinder containing a close-fitting screw, which forces the rubber stock fed at one end through a die at the other end, thus forming shapes such as treads, pipes, etc. The tuber is jacketed to permit heating and cooling, and extruded stock is usually cooled by passing through water.

Automobile Tires and Tubes. Approximately 72 per cent of all rubber is used in automobile tires and tubes. Fundamentally, an inner liner merely confines an air cushion, while the tire prevents the tube from leaking, protects it from abrasion and holds it on the wheel. Since they are the most important items of the rubber industry, tires and tubes deserve special mention.

At 60 miles an hour, the ordinary tire is flexing some 12 times per second and the automobile engine is putting one-third of its power into heating the tires. The only construction that has been found to give reasonable life under such conditions is that of cord fabric, that is, fabric of heavy cords with very few light cross-threads or none at all (pickless), embedded in fairly soft rubber. The cords are coated on both sides with

FIG. 210.—Cross-section of a Dunlop 6.00-16 four-ply automobile cord tire for passenger cars. At the top, note the tread, the non-skid grooves, the breaker strip under the tread, and the gum strips shown in black to right and left of breaker strip. Down the side walls the four plies are well shown, and at the bottom the bead wire wrapped first in the flipper, then the plies. A chafing strip is shown at the bottom, with the toe marked as a black triangular dot. (Courtesy of Dunlop Tire and Rubber Company, Buffalo, N. Y.)



by calendering, cut on a bias angle of 45 to 55°, and built into a tire carcass on a drum or collapsible core. "Beads" of wire imbedded in rubber are attached at the edges of the fabric bands to give rigid support to the rim of the wheel (Fig. 210). "Flippers" and "chafing strips" used around the bead "tie-in" are of light square-woven fabric friction-coated with rubber. The top-center of the carcass is protected by "breaker strips" of open mesh (leno) fabric, or of cords heavily coated with rubber, and a slab of tough abrasion-resisting stock which forms the sidewall. The sides are protected with thin slabs or "sidewalls."

Cotton has been universally used for cord fabric, its flexibility permitting high-speed travel with little danger of blowouts, or separation. With synthetic tires, however, as are necessary for truck or bus operation, heat is generated so rapidly that the inside of the tire may reach 325° F. or more. At these temperatures, cotton has only half its normal strength, and a blow-

out may result. Recent years have seen the substitution of "endless" thread for cotton "staple" fibers, and the resulting tires have far greater resistance to heat. The present trend is toward the use of rayon for large tires that are to be operated at high speeds, and for the better grades of passenger tires.

Passenger tires are built on a flat drum and shaped after removal from a vacuum chamber. Truck tires, being much thicker, are built on a collapsible core. After removal from the drum or core, the inside of the tire is coated with a non-sticky talc or mica composition, and an "air" bag, resembling a very heavy inner tube, inserted. Steel rings, or "curing rings," are clamped to the tire at the bead to support the airbag at its inner ends.

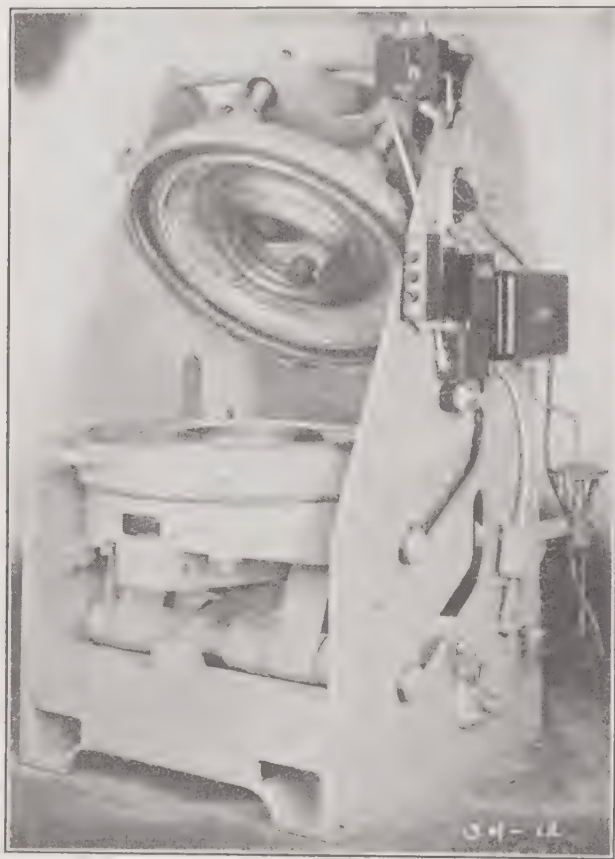


FIGURE 211.—An individual press of the latest design (1937) for curing automobile tires, also called a "watch-case" mold. The moldings are hollow to permit steam circulation. The mold opens automatically at the proper time. For inner tubes, the same type press is used, but with a smooth wall facing the rubber. (The Summit Mold and Machine Co., Akron, O.)

and the tire is placed in a two-piece cast-iron or forged steel mold which has the lettering, numerals and tread design in reverse. This mold may be of the individual, or "watch-case" type, having a jacket through which it is heated by steam, or it may be simply a movable mold of which 18 or 20 are stacked on a hydraulic ram inside an autoclave, where they can be heated by hydraulic pressure and heated by steam introduced around them. Air, and sometimes steam and hot water, are introduced into the airbag by flexible connections of copper tubing, expanding the tire carcass and causing the tread rubber to flow into the desired designs. The mold is then heated by steam for a specified time and temperature, such as 40 minutes at 307° F.

C1), to produce vulcanization. The steam is then shut off, the air in the mold opened, the airbag removed and the tire sent to the final finish.

A automobile tire shown in Figure 210 weighs 22 pounds, and contains pounds of rubber.

Rubber tubes were formerly cured on a steel or aluminum mandrel and after curing, but now are usually spliced before curing and cured in a "match-case" mold on pressure applied through the valve. The cure is short, usually about 6 minutes.

Rubber Belting. Rubber belting is of much industrial importance, both for driving machinery and for conveying materials. Coated fabric is folded over in Figure 212, layers being added until the desired thickness is reached. A sheet of cover stock, properly compounded to resist abrasion for service, is then applied around the whole, and the belt cured in a rotary press under hydraulic pressure totalling usually not over 300 sq. in. of belt in the press. Stretching devices are often used to keep the belt in tension during vulcanization.

FIGURE 212.--Arrangement of canvas layers in a rubber belt for driving conveyors (cross-section).



Lead Hose. Seamless tubing of compounded rubber is extruded, and passed through the center of a loom which weaves on a covering of

This, in turn, becomes the core for a second seamless rubber tube. The cover of cotton threads, and final cover of seamless tubing. This last becomes the core for a seamless tube of lead, which is extruded by hydraulic pressure from a "lead press" carrying molten lead. The die through which the tube is passed is cooled so that the lead-covered hose is set with the lead somewhat below its melting point. The hose is then wound on a reel, placed in an autoclave, hydraulic pressure applied inside the hose, and steam introduced in the autoclave to produce vulcanization. When the pressure is released, the lead removed by a stripping machine, the hose cut into lengths and couplings attached.

Rubber Heels. The rubber for *rubber heels* is cut from sheets by means of a die, placed in a mold and cured between steam-heated platens. The cure is usually about 15 minutes at 307° F. (153° C.). Tan heels are colored with red iron oxide. The rubber contains considerable filler so that the heel can be properly finished. To give some idea of the volume of this item, one plant is said to produce regularly 300,000 pairs of heels per day.

Balata. This is a gum of importance in the rubber industry, for it is a combination with rubber for golf balls. The crude balata is purified by extraction in naphtha, filtration, and evaporation, yielding the wax-like, **white gum**.

Golf balls are made by hot-pressing two hemispheres, then placing a core of ammonium nitrite inside, and cementing the two smoothed edges together with rubber cement, with heat. The ball is thus sealed, and the nitrogen

from the nitrite forms its inner gas. Two shaped pieces of felt are glued for the covering.

Gaskets. Compounded rubber from the mixing rolls is cut to approximate circular size by means of very small, rapidly rotating knives. The knives are so thin that when whirling they are not visible. The rubber cut is weighed and placed in the mold and cured. On removal from the mold the excess rubber is trimmed off by hand and the finished gasket in proper form and corrugations is ready for use. Small gaskets are stamped out.

Rubber Flooring. Flooring is usually made with a tiled effect. To produce this, squares or other shapes of the different colors are cut from structured sheets, assembled to form the proper design, and placed over a sheet of black rubber. The whole is then vulcanized under the usual pressure with steam heat to form a single piece of rubber, extremely durable and easy on the feet. Such flooring is used by the Pullman Co. and in many public buildings.



FIGURE 213.—Pouring compounded latex froth into molds during manufacture of cellular air cushions. (Courtesy of Dunlop Tire and Rubber Co.)

Hard Rubber. Most soft rubber articles contain only some three per cent of sulfur on the rubber. Between about 7 and 30 per cent sulfur is an intermediate zone which gives products of little commercial value, due to stiffness, poor aging, etc. If 30 to 50 per cent sulfur is used, hard rubber results. Because of an exothermic reaction between the sulfur and rubber, thick articles of hard rubber have to be cured at low temperatures for long periods of time to prevent porosity or "blowing." Most hard rubber com-

contain lime or magnesia. Organic accelerators are useful in some articles, but cannot reduce the time of cure to make it comparable with rubber. Hard rubber cures range from 30 minutes to 4 hours, which makes the cost of curing much higher than that of similar articles of synthetic resins, so that in this respect, hard rubber is at a disadvantage.



FIGURE 214.—Trimming vulcanized and dried cellular rubber cushions, made from latex. (Courtesy of Dunlop Tire and Rubber Co.)

Cements and Doughs. An unvulcanized rubber compound can be swelled with soline or benzol, and by successive additions of solvent and working over, converted into a viscous dough or cement. Such cements are used to unite rubber surfaces in preparation for vulcanization, and as adhesives for special uses. The thicker doughs are used to spread on, and thus form a layer of rubber, fabrics that are too light to stand calendering in the ordinary manner. Hospital sheeting and rubberized gingham are made in this way. The coated fabric, after the solvent has evaporated, being rolled in a drum, protected with an outside rubber wrap, and cured in steam.

Latex. Rubber latex itself is now used in large quantities; it is shipped directly from the plantation to the consumer in drums, and even in tank steamers, with the addition of ammonia to preserve and stabilize the emulsion. The raw latex may be concentrated by creaming, by centrifuging, or by evaporating off the water after addition of a stabilizer, or in a vacuum. Sulfur, accelerators, and other compounding ingredients may be added by using protective colloids.

Latex balloons, gloves and other thin objects are produced by dipping forms in such compounded latex. Thus, to make the rubber gloves

used for protection in acid plants, a porcelain form the shape of a hand is coated with calcium nitrate-glucose solution, and dipped into concentrated latex. A deposit forms in the exact shape of the hand; after it is thick enough, the form and glove are plunged into warm water for curing, after which the glove may be stripped off. The whole operation from beginning to end is a matter of minutes. By making the form the anode in an electrolyzing cell, thicker coatings may be formed. This process is called **trodeposition**.

Sponge Rubber. Sponge rubber may be made by incorporating ammonium carbonate or stearic acid and sodium bicarbonate in a very soft rubber stock. The heat of vulcanization releases NH_3 and CO_2 which is absorbed by the compound to a spongy mass, the size of the pores depending on the amount of gas, the softness of the stock and the rate of vulcanization.

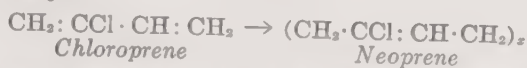
Sponge rubber, or cellular rubber, is also made from latex. To it has been added a frothing agent (such as castor oil soap) and into it subsequently air has been beaten. A slow-acting coagulant is then added and the whole poured into forms (Figs. 213 and 214). The delayed coagulation allows some 10 minutes for the pouring. The coagulated mass is cured by immersion in hot water for some 20 minutes, removed, washed and dried with gently warmed air. The volume of air in this type of sponge rubber is 4 to 5 times that of the rubber. The upholstery in the streamlined trains is mostly sponge rubber.

Reclaimed Rubber. Scrap vulcanized rubber may be reclaimed to produce a product which is an auxiliary to crude rubber in the manufacture of many types of goods. The largest source of scrap is worn-out tires, which are reclaimed chiefly by the alkali process developed by A. H. Marks in 1898. Beads are removed from the tires, and the remaining carcass finely ground and digested in 4 to 8 per cent caustic soda solution at 160 to 200 lbs. pressure for 8 to 24 hours depending on the type of tire, truck tires taking longer. Oils and swelling agents may also be added. This digestion removes all free sulfur, destroys the fabric and partially depolymerizes the rubber, which is then washed, dewatered, dried, and "refined" by several passes through a refiner. The latter is similar to a two-roll mill, the rolls only 30 in. long and set very tightly together. The final sheet comes from the refiner .002 to .005 in. thick, and is collected into a slab on a drum. The use of reclaim fluctuates with the price of rubber, annual consumption varying between 20 and 50 per cent of that of crude rubber. The shortage of rubber has rendered the maximum recovery of reclaim of the utmost importance; it is hoped that 350,000 tons per year may be realized (June, 1942). Such an amount might permit the use of reclaimed rubber for manufacturing tires for civilians, though they could not safely be operated at more than 35 miles an hour.

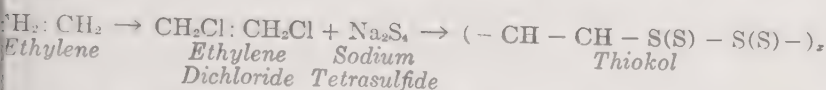
SYNTHETIC RUBBERS

Natural rubber is a polymer of isoprene, $\text{CH}_2=\text{CH} \cdot \text{C}(\text{CH}_3)=\text{CH}_2$, a colorless liquid, boiling point 34°C . Depending on the type and extent of mastication, rubber as compounded is estimated to have a molecular weight ranging from 25,000 to 180,000, corresponding to polymers of

2600 isoprene molecules. So far, all attempts to synthesize isoprene derive from it polymers of commercial value have been unsuccessful. During World War I, about 2000 tons of a synthetic rubber of low quality were made in Germany from dimethyl butadiene, $\text{CH}_2:\text{C}(\text{CH}_3):\text{CH}_2:\text{CH}_2$. Experimental work was also carried on in England and Russia. After the war, interest in synthetic rubbers subsided until when active research was begun by the DuPont Company. This led in the appearance of neoprene in 1931. This is a polymer of isoprene (boiling point 59.4°C .), which in turn is derived from isoprene and chlorine. Though more expensive than natural rubber, it has much better resistance to oils and sunlight; hence it is especially useful for gasoline and oil-loading hose. In 1941, about 6300 tons of the various types of neoprene were produced, and capacity is being rapidly increased.

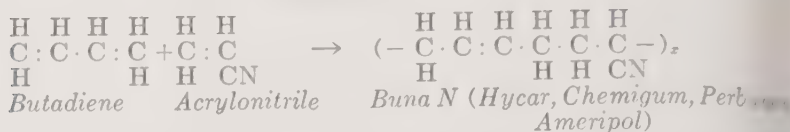
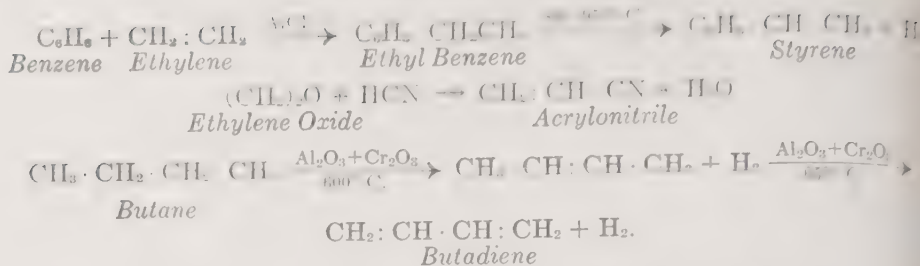


In 1932, Thiokol, so named from the Greek *thion* (sulfur), formed by the action of an organic dihalide with sodium tetrasulfide, was introduced commercially.



It is the most oil-resistant of all the synthetic rubbers, and has fair tensile strength as well. Its chief use is in gasoline hose linings, and in other products such as self-sealing gasoline tanks, which come into direct and prolonged contact with hydrocarbon solvents. Several types have been made commercially, and present production facilities are being vastly increased to meet military demands.

Simultaneously, research was going forward in Europe. In 1935, commercial production of synthetic rubbers from butadiene was announced by I.G. Farben. These were called "Buna" rubbers; the name is derived from the first syllable of "butadiene" and the chemical symbol for sodium, Na, which is involved in the reaction. The "S" and "N" designations stand for sulfur and nitrogen respectively. Since 1940, development of several modifications has been rapid in Germany. Following technique developed in the industry of synthetic resins, it was found possible to copolymerize several compounds with butadiene to give better products than the latter alone. Styrene, styrene and acrylonitrile are chiefly used. These may be mixed with butadiene in varying proportions, and are emulsified with water with the aid of a soap and polymerized with catalysts, usually by heating at $60-70^\circ\text{C}$. for 10-15 hours. Modifying agents such as carbon tetrachloride, carbon disulfide, etc., are added to control the reaction. The resulting product is coagulated with an acid, washed, sheeted and dried, an inhibitor such as phenyl-beta-naphthylamine usually being added to stop further oxidation. The main reactions are shown below, but several others are also used.



Buna S is a copolymer of styrene and butadiene. It most nearly duplicates the properties of natural rubber, both good and bad.

Butyl rubber, a copolymer of butadiene and isobutylene, is not yet marketed commercially, but tests carried out under service conditions indicate that it is a promising material for low-grade tires.

It should be noted that of these many possible synthetic rubbers, or plastics, each is but a raw material to be compounded, just as natural rubber is, to give a wide range of properties. Neoprenes vulcanize without the use of sulfur, but require the presence of metallic oxides, chiefly zinc oxide. The Buna rubbers use sulfur, but require special plasticizers to permit satisfactory handling. Germany, having little available petroleum, makes synthetic rubber from limestone and coke through acetylene. The United States finds the gases from petroleum cracking convenient raw materials, but could accomplish similar results by using alcohol obtained from grain and other agricultural products, if this were found to be economically desirable. This method has been successfully used in the Soviet Union for several years. Most synthetic rubbers have better resistance to oils, sunlight, and oxygen than natural rubber, and about the same abrasion resistance and other properties necessary in tires.

Comparison of Properties of Synthetic Rubbers*

Rubber	Yields soft or hard rubber	Chemical Resistance	Oil Resistance	Electrical Properties	Abrasion Resistance	Heat Resistance	Cold Flow Resistance	Aging
Natural	All hardnesses	Good	Very poor	Good	Good	Medium	Good	Fair
Neoprene	Soft only	Good	Fair	Fair	Good	Good	Fair	Good
Buna N	All hardnesses	Fair	Excellent to aliphatic hydrocarbons	Fair	Good	Good	Good	Good
Hycar O.R. ...	All hardnesses	Fair	Outstanding toward aliphatic oils	Fair	Good	Good	Good	Good
Thiokol	Soft only	Good	Excellent toward aro. and ali.	Fair	Poor	Poor	Poor	Fair
Butyl	Soft only	Excellent	Poor, fair to vegetable oils and fatty acids	Excellent	Fair	Excellent	Fair	Fair
Buna S	All hardnesses	Good	Poor	Excellent	Good	Good	Good	Good

* Chem. Met. Eng., March, 1942.

This book goes to press, a huge synthetic rubber program is being taken both by private and Government funds. It is planned to increase the production of four types (neoprene, Thiokol, Buna S and butyl) total of from 800,000 to 1,000,000 tons a year. This goal will probably be attained until 1944. Many new plants are under construction, and it is hoped that the United States will eventually become independent of all sources of natural rubber, now almost completely cut off by the war.

OTHER PATENTS

1,749, a compounding process for increasing the resistance of rubber to deterioration due to aging by incorporating a monohydroxy anti-oxidant having the general formula $\text{HO}-\text{R}-\text{R}_1$, where R and R_1 represent aryl radicals, at least one of which is an aryl grouping; 1,797,250, process for manufacture of transparent and vulcanized rubber; 1,880,528-9, the reaction product of nitrosaphthol and mercaptathiazole as accelerators; 1,832,163, accelerating the vulcanization of rubber by vulcanizing in the presence of carbisopropoxythione disulfide; 1,869,172, compounding rubber, using an aryl residue from the purification of light oils; 1,862,334, a stock fabricating process for making pneumatic tires; 1,859,337, a vulcanizing mold for inner tubes; 1,844,414, a vulcanizer for retreading automobile tires; 1,826,901, reclaiming waste rubber; 1,797,243 and 1,806,388, rubber dispersion with potassium oleate; 1,755,891, treating coagulated bodies by introducing clay, mixing, and removing the clay by means of water (W. B. Pratt); dispersing by means of a solvent, 1,621,468; by means of a soap, 1,732,027; by means of a colloidal substance, 1,731,725; 1,874,546, process of latex emulsion; 1,885,154, process to produce a concentrated and purified latex; 1,850,673, reducing the alkalinity of latex by treating with silica gel; 1,847,717, a creaming agent for latex; 2,029,410, on chemical products and producing Neoprene to Wallace H. Carothers, Arnold M. Collins, James E. Kirby, with 10 claims; 2,002,622, on stabilizing latex; 2,279,293, on a new synthetic rubber from butadiene and isobutyl acrylate.

PROBLEMS

1. In the analysis of a rubber compound, the rubber is first treated with acetone to remove or extract the "free" sulfur, and then the sulfur which is "combined" with the rubber, or one of the admixtures, is determined in the residue by means of iron for example, or by oxidation, leading in either case to a precipitation of barium sulfate. In a sample under study, the acetone extract is found to contain 10 per cent free sulfur on the weight of the sample. The extracted sample is found to have 3.1 per cent sulfur based on the weight of the extracted sample. What is the percentage of "combined sulfur" in the original sample? (b) What percentage of the "combined sulfur" if the original sample contained 5.0 per cent of opone (29.0 per cent ZnS , 71.0 per cent BaSO_4)? Note: BaSO_4 in the lithopone is precipitated off along with any insoluble residue after oxidation, while the ZnS is left in solution.

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7. "A new plastic material AXF," used among other ways as a compounding ingredient in the manufacture of neoprene, and also on the ethylene polysulfide plastic known as Thiokol, S. D. A. E. Brooks, and G. H. Cady, *Ind. Eng. Chem.*, 28, 275 (1936). Made from ethylene dichloride and aromatic hydrocarbons of formula $\text{R} \cdot \text{C}_6\text{H}_4 \cdot \text{R}$, in presence

- "Acetylene polymers and their derivatives. II. A new synthetic rubber: chloroprene and its polymers," Wallace H. Carothers, Ira Williams, Arnold M. Collins and J. E. Kirby, *J. Am. Chem. Soc.*, 53, 4203 (1931).
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Note supplementing data on synthetic rubber. July 10th, 1942. The present government program projects plants with a total capacity of 800,000 tons of rubber, mainly Buna S, a year, from raw materials derived from natural gas, petroleum products and acetylene. The main raw material will be butadiene made from butane, but also obtained as by-product in the manufacture of aviation gasoline by catalytic cracking. 9.6 pounds of butadiene and 2.4 pounds of styrene produce 12 pounds of rubber. Butadiene will cost about 10 cents a pound, once full capacity is reached. The Buna S rubber is expected to cost 20 cents a pound, again once the full capacity is reached. The date for the plants to be in full operation is August 1st, 1943. An additional 200,000 tons made with grain alcohol as the raw material is being planned.

correct appraisal of what advantage may be derived from the patent and a knowledge of their dangers and limitations, are an essential part of the education for the future chemical engineer and industrial chemist.

Chapter 40

Patents

A patent is a publication, a disclosure, for the benefit of the public, of an invention of new and useful matter.

A patent is granted by the government in consideration of the disclosure of a new process, machine, or method which may be applied to practical use. The purpose of granting patents is to encourage the development of the practical arts. The disclosures disclosed by patents are for the ultimate benefit of the public. The patent law offers an inducement for creating inventions, and for divulging their secrets. It offers the inventor a monopoly for a limited period.

A patent may be a doubtful gift, since the burden of enforcing this monopoly is placed on the inventor, and infringement on the inventor's patent must be discovered by him, and unless the infringer settles or ceases his infringement, suit must be brought in the Federal courts and prosecuted by the inventor. The law is passive; if the patentee succeeds in proving the infringement, the courts will grant an injunction during the life of the patent and award damages and profits. Frequently it is difficult to prove that there is an infringement, particularly for the chemist patentee. Usually chemical plants are closed to public inspection. However, if there are substantial grounds for believing that there is a case of infringement, the courts will compel the alleged infringer to disclose fully. If the invention is on a chemical product which can be made in only one way, the proof is simpler; but such articles are few. As a rule, the products are made in a number of ways, so that the mere selling of a product proves nothing. The infringement of a patented automobile is comparatively easy to determine, since the invention must appear on public highways; similarly a new and improved type of cardboard egg container, necessarily must appear in public, and the question of infringement is comparatively simple to determine. This is not true with the average chemical patent; the infringer may hide his process behind factory walls; the article put on sale may reveal nothing as to its method of manufacture. For this reason, not infrequently chemical processes have been kept secret.

Keeping a process secret, however, also involves risk; an unfaithful employee or partner may take out a patent on such process and force the discoverer to pay tribute on his own discovery. This may seem a violation of law, but the fundamental principle of the patent law is that every discovery shall be made public for the benefit of everyone, and whoever chooses to keep the invention secret must do so at his own risk. A process based on a secret process is unsafe, unless the secret is so thoroughly guarded as to substantially preclude the possibility of outside parties discovering it.

It goes without saying that no reputable business house will consciously infringe, but will gladly give to inventive ability due recognition and reward. The danger of loss of the monopoly comes from the acts of individuals or corporations in business whose policy is determined by greed rather than principle.

The patent law is rooted in the Federal Constitution and is defined by Congressional statutes.¹ Its purpose is to obtain for the benefit of the public valuable information which will advance the practical sciences and arts which otherwise might be lost on the death of the inventor. The law is primarily good for the public and, for a limited period, protects the inventor.

STATUTORY CLASSES OF INVENTION

The patent statute divides patentable subject matter into four classes, viz., arts, machines, manufactures, and compositions of matter.

1. The word "art" in the statute includes the substantially synonymous terms "process," "mode," and "method." This term includes an act or a series of acts which may be carried out, by hand or otherwise, without reference to any special mechanism, such as the art of dyeing or steel making. The mere function of a machine cannot be patented as an art or process. It is under the heading of an art, method, or process that many chemical patents are granted, although some are granted as compositions of matter.

2. A "machine" is usually a combination of mechanical parts which are adapted to receive, transmit, and modify force or motion to do useful work.

3. The term "manufacture" covers articles or fabric made as finalities and thus distinguished from machines by not having any rule of action, and from compositions of matter by not involving the relation of ingredients. Examples are a chain, a lamp, or a chimney.

4. A "composition of matter" is a compound of two or more ingredients forming a homogeneous whole, such as paint, glue, ink, or a dye.

PATENTABILITY

The subject matter of a patent must involve invention; it must be new and it must be useful.

(a) The question as to whether a creation is an invention is largely a question of fact. No court has been able to give a general positive definition of this term as used in the patent law. Many rules have been made for testing the question of invention, substantially all of which are negative, but they nevertheless serve as guides in most cases as well as positive rules. Some of such rules are:

1. Mere mechanical skill is not invention.
2. Excellence of workmanship is not invention.
3. Usually the substitution of one material for another is not invention; thus wood is replaced by aluminum, Bakelite, or iron, this does not constitute an invention unless such substitution produces some new and unexpected results.
4. A change of size is not invention.
5. A change in degree or form is not invention.
6. An aggregation of parts which does not interdependently co-operate to produce a useful result is not an invention; thus the courts have held that a rubber-lead pencil cannot be patented, since the lead and the rubber are not simultaneously used.
7. Mere duplication of parts is not invention.
8. The omission of an element is not invention.

¹ Article 1, Section 8; the Patent Office was established by Act of Congress in 1790; the first patent was a chemical one, for a process for making potash and pearl ashes (U. S. Patent 1, to Samuel Hopkins, July 31, 1790).

the substitution of an equivalent is not invention. The breadth of patent depends largely upon the interpretation of equivalents. In general, it may be said that an invention which is a mere modification of an established art, or a combination of two or more inventions will have a much greater range of equivalents than an invention involving only a small advance in an established art. Doing an old thing for a new and analogous purpose is not invention.

In a decision made in 1941, the United States Supreme Court held "that the test of patentability is whether a 'flash of creative genius' is revealed by the alleged invention. The High court proclaimed that, unless a strict application of this test reveals the presence of such a flash, a patent is refused for want of invention."² This important and perhaps disturbing statement has caused much discussion.³ It is at least a positive statement regarding what constitutes invention. If it is interpreted reasonably, many patents would be ruled valid today than may seem at first sight. Several means of evaluating this quality have been used by the courts in the past; there has been deemed to have been invention when (1) the invention was unexpected; (2) long experimentation had been required; (3) the invention, until then vainly sought by others, was taken, which turned all the previous steps into a success; there are still others.

An invention must be new. This means that the invention must not have been the subject of publication anywhere in the world prior to the date of invention here, and must not have been in use in the United States prior to such date of invention. Foreign patents are called publications. Therefore, no valid United States patent can be granted for any invention described in patents issued in foreign countries.

Anticipation is not negated by abandoned experiments; if experiments have been performed, and then dropped, even though partially or accidentally performing the function desired, such experiments will not anticipate a later perfected invention. If, however, such experiments are continued and a patent application is filed in the Patent Office within two years after the first public use, a valid patent may be secured.

Accidental production is not an anticipation and does not destroy the novelty of an invention. Prior use of an invention in countries foreign to the United States is not an anticipation; but a prior domestic use is an anticipation.

The invention must be useful in the industrial arts. This limitation automatically rules out many freak inventions which would consume the time of the examiners and give nothing of value to the public. An invention which is a mere combination or process, which will not answer the purpose for which it was intended without redesign or alteration, is not an invention. A scientific principle cannot be patented; a useful application of it to the industrial arts must be presented. Likewise the principle or function of a machine cannot be patented.

Patent Applications. All patent applications must be filed with the Commissioner of Patents at the Patent Office,⁴ Washington, D. C. A preface states the object of the invention; this is followed by a description of the invention, which must be full, clear, concise, and exact enough to

² Taken from the article "Flash of Genius"—"Patent doctrine and the chemist," by Thomas H. Crompton and Engineering News, 20, 523 (1942).
³ See also "The Patent Office in 1940 and 1941," by Nelson Little, Ind. Eng. Chem., 34, 88 (1942).
⁴ 35 U.S.C. 101, 102, 103, 104, 105, 106, 107, 108, 109, 110, 111, 112, 113, 114, 115, 116, 117, 118, 119, 120, 121, 122, 123, 124, 125, part of the Department of Commerce.

enable any person skilled in the art or science to which it pertains, or which it is connected most closely to make and use the invention. If it is a machine, the description must be exact enough to enable its manufacture; if it is a composition of matter, the description must be clear enough to admit the compounding; if the invention is a process, the method of carrying it out must be clearly described.

The claims follow the description and point out the novelty of the invention. For each novel part, a distinct and formal claim is necessary. Patents are not granted except for those novel disclosures which are distinctly claimed. The monopoly granted is limited to the contents of the claims.

The application is accompanied by an oath made by the inventor, stating forth that he is the sole inventor (or if more than one, that they are the sole joint inventors), that he does not know and does not believe that his invention was ever known before his discovery thereof, or patented or described in any printed publication in any country before his discovery thereof, or more than two years prior to his application, or in public use or on sale in the United States for more than two years prior to his application; and further that his invention has not been patented in any country foreign to the United States on an application filed by him or on his authority more than twelve months prior to his application.

Whenever drawings will make the disclosure clearer, they must be presented with the application. In former years, models were required, but they are not any longer.

The fee due on the patent application is \$30 when filed, and the fee for issuing the patent is \$30. The fees for design patents vary according to their term.

Patent Office Actions. On receipt at the Patent Office, an application is given a serial number and then goes to one of about fifty different divisions, each one of which handles a single group or a series of related groups of inventions. Each of these divisions is supplied with copies of all domestic and foreign patents and most of the publications on the subjects handled in that division. Each division has one head or principal examiner, and a number of primary or assistant examiners. If the application is rejected because of prior publication or technical defects in the form of the application, a letter of rejection is returned to the applicant or his attorney, setting forth succinctly the reasons for rejection. The applicant or attorney must secure copies of all references cited by the examiner, and has one year from the date of the office action in which to amend his application, or point out to the examiner the differences between the disclosures of the publications referred to and his own invention. The wording of the original application may be changed by amendment, but the applicant is not permitted to add any new matter. If the application is twice rejected on the same grounds, such rejection is made final; the applicant may then appeal to the Board of Examiners-in-chief of the Patent Office; from the board, he may appeal to the Commissioner of Patents; from the Commissioner's decision, he may appeal to the Circuit Court of Appeals of

dict of Columbia. The decision of the last-named court controls the action of the Patent Office on the matter at issue.⁵

Interferences. It sometimes happens that two patent applications for substantially the same invention are pending in the Patent Office at the same time. An interference is a proceeding instituted for the purpose of determining the question of priority of invention between two or more persons claiming substantially the same patentable invention. Patents are granted to the first inventor. The fact that one of the parties to an interference proceeding has already obtained a patent will not prevent an interference, for, although the Commissioner has no power to cancel the patent, he may grant another patent for the same invention to the person who is to be the prior inventor. The first inventor to file his application in the Patent Office is the senior party to the interference. The burden of proving the date of invention is upon the party who last files his application. If he succeeds in overcoming the date of the filing of the first party's application, then the burden of proving priority of invention shifts to the first filer. Priority is determined by proof of a series of facts, as:

- the date of the conception of the invention;
- the date of the disclosure of the invention to another person;
- the date of the first drawings, if any;
- the date of the first model, if any;
- the date of the first reduction to practice, such as the commercial operation of the invention; the date of filing a patent application is in the patent law a conclusive reduction to practice.

The importance of keeping properly dated memorandum books, or notes, or other proof concerning the invention will at once be apparent to every young chemist.⁶

If there are no rejections, or if the rejections have been overcome, and no interferences have been found, the applicant is notified that his patent may be allowed; he is then given an interval of six months within which to pay the final fee for issuing the patent. All patents are issued on Tuesdays. If the final fees are paid on or before a Thursday, the patent will be issued on the fourth Tuesday thereafter.

Searches. Much information as to the advisability of patenting an invention may be obtained by means of preliminary searches. Such searches may be made for the purpose of determining in advance the patentability of proposed claims, or whether the invention would infringe existing patents if commercially exploited. These searches are never performed

A bill to establish a Court of Patent Appeals was introduced in the United States senate in 1937, by Senator McAdoo. The court would have exclusive appellate jurisdiction to review the final decisions of the district courts; it would have three permanent scientific advisers. The United States Department of Agriculture had filed suit (on March, 1932), with the United States Court of Customs and Patent Appeals, contesting the validity of U. S. Patents 1,787,316 and 7,117,316, issued to Alfred Wohl, of Germany. The patent 1,285,117 issued to Gibbs and Conover in November, 1916, was cancelled by the Court of Appeals at the time the Wohl patents were issued. The date of the date of "reduction to practice" in the case of each invention became the determining factor. The date for Gibbs-Conover is September 7th, 1916; for Wohl, either September 4th or 9th, depending upon the interpretation of "reduction to practice" by the court. In March, 1934, the court decided priority to Wohl, and declared the Wohl patents valid. The original application to the Patent Office by Wohl, of June 28th, 1916, was amended by him on September 4th and again on September 9th, 1916, listing the higher temperature, 350 to 550° C., which had been also stated by Gibbs. The court decided that Wohl was entitled to a date for reduction to practice at least as early as the date of the filing of his amendment. Nothing sold earlier than September 4th could be shown by Gibbs. This case brings out the importance of the availability of proofs of date and hour of reduction to practice."

by the Patent Office until after the patent application is filed, but they can be obtained through attorneys who are skilled in this work. In the Patent Office all domestic and foreign patents are classified according to their subject matter. There is no other place where such a classification can be found. It is, therefore, essential that such searches be made in the Patent Office by those who are familiar with the classification.

Patentability searches are made to determine whether an invention is novel and patentable. Such searches are made among the issued patents and reports upon them are usually accompanied by a few selected copies of the patents closest to the invention searched. Such a search determines the advisability or inadvisability of filing a patent application. The cost of such searches varies from \$5 up. The search made by the inventor through complete files of patents usually wastes much time and is inconclusive, since the files of patents in the libraries are not classified and many pertinent patents may be overlooked.

A determination of whether the invention has been in public commercial use is difficult to make. The knowledge of the commercial men of the art is frequently valuable in determining this question, but sometimes a restricted public use may have been made and not be known to those familiar with the general trade. If the invention has been in public use, even though such use is restricted, for more than two years, it will invalidate any patent granted on the invention.

Validity and infringement searches cover substantially all of the patents which come within the scope of the invention in question and are made in order to determine, as positively as can be done, whether the proposed patent, if granted, would be valid, and the invention, if commercially made, would infringe prior patents. Such validity and infringement searches are usually quite expensive and frequently cost several hundred dollars. It should be noted that the Patent Office merely determines the question of novelty and does not attempt to determine the question of possible infringements of prior patents; the grant of a patent does not guarantee the inventor that his invention is free from the dominating influence of a prior patent. In expensive commercial operations, therefore, validity and infringement searches are quite important.

Title. The monopoly granted by the patent belongs to the inventor; it is property and the title is vested in him. Such title is absolute and unqualified; the Federal Government cannot take it away from him; the State cannot interfere. Only a court in bankruptcy can pass title to a patent without the written consent of the patentee; a receiver in a State court may administer a patent but cannot transfer the title.

The monopoly granted by the patent is legally transferable. The patentee himself may pass title to any other person or to a corporation, but he must do so by means of a written assignment. In order that an assignment shall be legally effective against a claim by strangers who did not know of such assignment, it must be recorded in the Patent Office within three months after its date. If such record is not made within the time stated, a subsequent assignee, not knowing of the first assignment, may secure a valid title to the patented invention, if he complies with the law.

according to his subsequent assignment, and, in that event, the only remedy of the first assignee is to sue the assignor for fraud.

The patentee, if he pleases, may refrain from making, using, or selling the invention and may decline to permit others to do so. The patentee may retain title to his patent, and grant licenses to operate and sell or use the invention under any desired expressed conditions or within certain territorial limits or for limited periods. The law does not require that licenses be recorded. Such licenses may be either verbal or written. Unless the patentee is a reputable person, the purchaser of the title to the patent may be required to show that previous licenses have substantially detracted from the value of the patent.

Period of the Monopoly. In the United States the patented monopoly lasts for seventeen years⁷ from the date of the issue of the patent, except that in certain cases patents are granted for a period of three and one-half years, or seven years, or fourteen years, as the applicant may elect. Many years ago the law provided that patent monopolies might be extended, but that provision has now been repealed and now no patent can be extended except by act of Congress. If, however, improvements on the original are made, such improvements may be protected by patent and thus frequently the monopoly is, in effect, continued for a longer period than the seventeen-year term of the original grant. The original patent may cover the disclosed invention only in a crude way; refinements come with practice, and such refinements may be protected. In many cases the protection on improvements would be without specific patents on such improvements, since the original invention during the seventeen years' monopoly may so improve the art that successful competition is not to be feared. Of course, such a condition does not apply in all cases.

Disclaimers and Reissues. An inventor may find, after his patent is issued, that he has claimed more than he originally invented or was entitled to. In such case he may prepare and file in the Patent Office a statement containing a disavowal or disclaimer of such excessive claims, retaining, however, that part of his invention which is truly his. The patent remains valid for the parts which are justly and truly his invention. Such a statement is called a disclaimer. The advantage of a disclaimer lies in the fact that the danger of invalidity is thus removed if the question becomes an issue in the courts.

A patent may be found to be invalid or inoperative because of inadvertent oversight, accident, or mistake without fraudulent or deceptive intent; in that case, it may be surrendered to the Commissioner of Patents, and, on proper showing, will be reissued in the corrected form. The statute does not state how long a period may elapse after the issue of a patent before a reissue must be applied for, but many decisions have held that a lapse of more than two years is fatal to the grant of a valid reissue.

⁷England, 16 years; Canada, 18; Belgium, 20; France and Germany, 15 years. A revision of the law makes the period 20 years after 1933. In Germany, the period is reckoned from the filing of the application; in this country, it is reckoned from the date of issue, an important difference.

The importance of not leaving out an essential and integral step in the original patent from the application is shown in a decision reported in *Chemical and Engineering News*, 20, 671 (1942).

Foreign Statutes. A United States patentee has the right to apply patents in countries foreign to this country. He must claim these rights within twelve months from the date of filing his application in this country if he wishes to preserve his original filing date; or he may file his foreign patent applications at any time before the actual issue of his patent in this country. If he does neither of these things he loses the opportunity of securing a monopoly in many countries. So far as novelty is concerned, the laws of substantially all foreign countries provide restrictions similar to those existing in this country. Most foreign patents, however, are subject to taxes and in many foreign countries manufacturing of the inventions must be done within a year or more after the grant of the patent in those countries.⁹ Unless the foreign taxes are paid and the foreign manufacturing requirements complied with, the patents in most foreign countries are thereby rendered invalid.

No taxes are payable on Canadian patents. In Great Britain taxes are payable only after the expiration of the fourth year of the life of the patent. There are more than one hundred and fifty different countries in which patent laws exist.¹⁰ The question of whether a foreign patent should be taken out depends largely on the subject matter of the invention, and the industrial condition of the country in question.

It should be here noted that an invention patented in a foreign country and not patented in the United States, may be legally made, used, and sold by any one in this country. Likewise, an invention patented only in the United States may be used by anyone in any country foreign to the United States without violating any legal rights of the patentee.

Infringement. Suits for infringement must be brought in the Federal District Courts by means of a bill of complaint. The defendant files an answer to the bill of complaint. Many defenses may be set up in the charge of infringement, such as anticipation by means of prior patents, prior publications, or prior public use, or on the grounds of insufficient disclosure, absence of utility, inoperativeness, or aggregation. Of course, proof of non-infringement is sufficient to cause the bill of complaint to be dismissed.

Prior to the trial of a patent suit in the courts, depositions of fact witnesses may be taken, providing such witnesses live more than one hundred miles from the place of trial. These depositions are taken by either oral or written interrogatories upon examination and cross-examination of the parties to the suit or their attorneys. After being taken, such depositions are filed with the trial court and become a part of the trial record. Experts giving depositions relating to the subject matter of the patent involved must give their testimony in open court. The court rules provide that if the court understands the matter and does not desire such experts, such expert testimony is not permitted.

A suit brought for damages, profits, and for an injunction is an action

⁹ This is a serious handicap for the American patentee; the foreign patentee who has registered his patent in the U. S. Patent Office is not required to manufacture here.

¹⁰ All countries do not have the same methods or rules for judging and issuing patents. French patents issue immediately and without examination, hence they serve as advance signals for patents in other countries, and their factual value is small. German and Dutch patents issue only after painstaking examination, so that they are more apt to be limited to genuinely novel subjects. The British patents and Canadian patents are about equivalent in stringency of judgment to the United States patents.

quity, and is tried before a judge without a jury; a suit to recover damages only, is tried before a judge and a jury. In former years, probably in 90 per cent of the successful patent suits, claims for profits and damages were waived because of the difficulty of establishing them; within the past few years, however, court decisions have modified the rules as to the burden of proof so that it is much easier for the plaintiff to establish proof of profits and damages and much more difficult for the defendant to escape claims for such profits and damages. Recoveries in patent suits are, therefore, much more common than formerly.

Shop Rights. If an employee in a manufacturing plant makes an invention while in such employ on the time and with the materials of his employer, and thereafter secures a patent on such invention, the company or individual owning the plant has what is known as a shop right or a shop patent; that is, the employer can make, use, and sell the patented invention in such plant without the consent of the patentee. The monopoly of the patent, however, outside of the plant, is still solely vested in the patentee. Frequently the employee assigns his patent to his employer and relies on the employer's fairness for his reward. In some companies a contract is made between the employer and the employee, and provides that any invention made by the employee, during the term of his employment, which relates to the business of his employer, shall become the property of the employer. In the case of such contracts, of course, the title to the invention can be legally transferred to the employer. Shop rights, however, under conditions named, even in the absence of a contract, remain with the employer.

Marking Patented Articles. If patented articles or the containers fail to bear the word "patented," or an abbreviation thereof, together with the date of issue of the patent, no damages or profits can be collected from infringers, unless proof be made that they have had actual notice of the patent. Usually the words "Patent applied for" or "Patent pending" are placed on articles of trade if patent applications have been made, but there is no provision of law requiring such marking, and such marking is regarded as a warning.

Patent Publications and Services. Annually the Patent Office issues an annual volume giving the names of all patentees of that year, and a list of subjects upon which patents have been taken out. Besides the collection of the full-text patent specifications, there is issued by the various patent offices a journal containing abstracts of the full specifications. The United States Patent Office publishes the "Official Gazette of the U. S. Patent Office," in which the abstracts are arranged numerically. In the Canadian specifications, there is published the "Canadian Patent Record." The Patent Office in London publishes the "Illustrated Abstracts of Specifications"; since January 1st, 1931, the British specifications are classified in 40 groups. A list of these groups with their equivalents in terms of previous classifications of 146 groups, will be found in the index volumes of the Abridgements, or may be sent for directly. The publications just mentioned will be found in many of the public

libraries in the United States, deposited there free of charge by the several Offices for the convenience of the public. Such libraries will usually have a complete file of the United States full-text patent specifications, also a gift from the Patent Office to the public. Full files of the patents specifications of all countries will be found at the Patent Office in Washington, and may be consulted by any one; given the number, the patent can be found since they are arranged numerically. On request and payment of a moderate fee, a photostat will be sent.

There is one more service offered which is of the greatest convenience. The Superintendent of Documents, Washington, D. C., will send for \$1 the "U. S. Manual of Classification of Patents." After studying it, a request may be addressed to the Commissioner of Patents that all patents in a certain class, or subclass, be sent on, as fast as issued, without further notice. For this service, a fee of \$1 per year per class is charged, plus the usual 10 cents for each copy. In this way, the subscriber receives at his desk every patent which pertains to his specialty without any labor on his part.

It will be well to note that the British Patents now have running numbers, beginning with January 1, 1916. Before that time, every year started with number 1, so that for British Patents it was necessary to give the year as well as the patent number; this is no longer necessary for the patents issued since that date.

Of special value to the chemists' world is the "Chemical Patents Index," covering the United States patents dealing with chemical and allied topics for the years 1915 to 1924. Two other sources of patents information in the United States patents may be mentioned; one is the bi-monthly *Chemical Abstracts* with monthly, yearly, and decennial indexes; the other is the "Annual Survey of American Chemistry."¹²

Beginning with January 1st, 1928, and with volume 22, *Chemical Abstracts*, published by the American Chemical Society, lists patents under the name of the assignee, in addition to the customary listing under the name of the patentee. This is a tremendous advantage for the reader, who often knows which firm is developing a certain patent, without knowing the name of the patentee.

Starting with January 1st, 1935, there is provided as Part IV of the index of *Chemical Abstracts* the numbers of the patents, for which abstracts have appeared, arranged in the order of the numbers, and grouped by countries.

British patents will be found abstracted in *Chemical Abstracts* or in the abstracts of the *Journal of the Chemical Society* (London). A classified collection of German medicinal and dye patents is the *Friedlaender*,¹³ while patents dealing with the inorganic chemical industry are classified and reviewed in the Brauer and d'Ans collection.¹⁴

Copyrights and Trade-Marks. Copyrights are granted under separate

¹¹ "Chemical patents index (U. S. 1915-1924)," E. C. Worden, New York, Chemical Catalog Co. Inc., Reinhold Publishing Corp., Vol. I, 1927; Vol. II, 1932.

¹² Published (began 1925-26), for the National Research Council, by the Chemical Catalog Co. Inc. (Reinhold Publishing Corp.), New York. (Series now discontinued.)

¹³ See reading references for Chapter 28.

¹⁴ *Fortschritte der anorganisch-chemischen Industrie*, by Adolf Brauer and J. d'Ans, in 8 volumes, published by J. Springer, Berlin.

gressional statutes for books, maps, periodicals, drawings, pictures, musical compositions, dramatic works, and the like. Such applications are made at the Patent Office, but to the Registrar of Copyrights at the Library of Congress, Washington, D. C.

Trade-marks are registered in the Patent Office under the trade-mark laws. Labels and prints are registered in the Patent Office under the copyright laws. The Registrar of Copyrights has sole jurisdiction of the registration of everything referred to in the copyright laws, except labels and prints. A label is defined as something applied to the goods or to the container; a print is not so applied, but serves separately as advertising. Both labels and prints must be distinctive in appearance, and must be the result of original creation.

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An industrial chemist must have an acquaintance with the appliances suitable for large-scale operations, as distinct from laboratory practice; the proper choice of the specific appliances depends upon such an acquaintance. It would be too much to say that the success of a process depends upon the proper choice of auxiliary devices, but its difficulties will certainly be greatly lessened.

Chapter 41

Appliances Used by the Chemical Engineer I. Pumps, Fans, Blowers, and Compressors

Pumps are used to move liquids from one point to another, frequently to an elevated point. The simplest pump is the trench pump, which has a short barrel, a piston moved up and down by a hand lever, and, mounted in the piston, a clap valve opening on the down stroke and closing on the up stroke. As the piston is lowered, a gallon or so of water passes through the valve to the barrel above the piston; on the up stroke this amount of water is pushed up and discharged through a lip to a runway.

For industrial purposes, pumps are operated by steam or electric motors or they may be belt-driven or gear-driven; the latter are known as "power pumps." The variety in principle and design is considerable. A classification might be made as follows:

1. **Reciprocating pumps**, in which the pumping element has a back-and-forth motion, may be further divided into piston pumps, plunger pumps, and diaphragm pumps. The piston pumps are double-acting, that is, each side alternately pushes or sucks; if there is one piston, it is simplex; if there are two pistons, working on the same suction and discharge line, it is duplex; if there are three, it is triplex. The discharge from the duplex pump is more even than that from the simplex. The valves are located in an enlarged portion of the suction and discharge lines.

The plunger pump has a closed, hollow cylinder as the pumping element. In the vertical type it is single-acting, but usually triplex; in the horizontal type two plungers may be placed, working opposite each other. The piston pump is usually steam-driven, with the steam piston on the main pump shaft; the vertical triplex plunger pump is usually a power pump.

2. **Rotary pumps** with direct action are those which push the liquid bodily; examples are the gear pump, the sliding vane pump, and the two-vane pump such as the Roots-Connersville. The rotary pumps with indirect action, impelling rather than pushing, hence imparting a velocity, are the centrifugal pumps; the impeller may be "open," or if the vanes are cast between two disks, "closed." A centrifugal pump may work singly, the usual practice in chemical plants, or in stages; each stage has its own impeller and casing.

3. **The acid egg** (see Fig. 3), often called a blow case, is also a pump in the sense that it serves to move liquids, and slurries, from one place to another; the driving force is compressed air, and its operation may be automatic.

A **ram** is a special type of pump in which the feed water itself supplies driving force.

Reciprocating Pumps. The structure and operation of the **piston pump** illustrated in Figure 215. On the stroke from left to right, the water pushed by the front end of the piston, valves *LP* are depressed, and water is made to the pressure line; valves *RS* are held shut by the pressure, so that the suction line is closed. In the meantime and on the same stroke, the crank end of the piston has drawn in water through *LS*, but

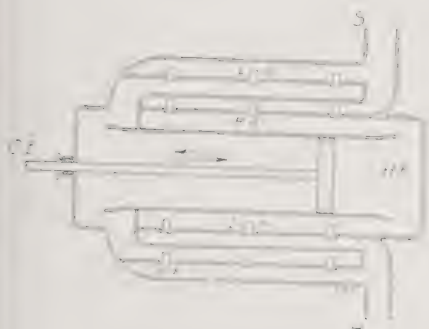


FIGURE 215.—Sketch of a double-acting piston pump. *CE*, crank end; *HE*, head end; *S*, suction line; *P*, pressure or delivery line. See text.

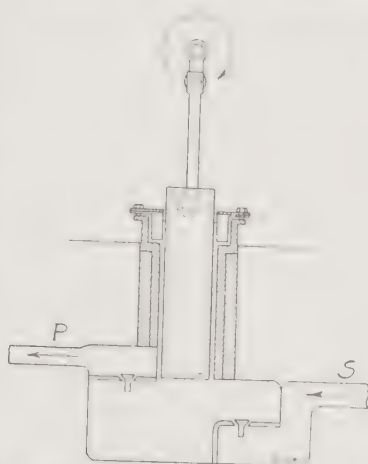


FIGURE 216.—A plunger pump; *S*, suction line; *P*, pressure or delivery line.

RP closed. On the return stroke, right to left, the crank end of the piston exerts pressure, forcing the valves *RP* open, and delivering the water to the pressure line; the head end of the piston on the same trip draws in water through *RS*, while *LP* stay closed. Such a pump would be double-acting.

The valve may be circular and may carry a rubber ring working on a metal seat; or ball valves may be preferred, consisting of a metal ball working against a metal seat, and fitted with shoulders which prevent their turning more than just enough to let the water through. Ball valves require no spring; they seat by their own weight; but flat valves are held shut by a steel spring, which is chosen so thin that it exerts just enough pressure to seat; the pressure is so weak that very little pressure by the water is it to unseat. The stem of the valve acts as a guide, causing it to seat properly. In the sketch of the piston pump, the springs holding the valves shut are not shown.

The **plunger pump** is shown in the adjoined sketch. The plunger is a cylindrical boot, with only one working side; hence it is single-acting. As shown in Figure 216, the plunger is at the end of the down stroke, and ready to start the up stroke. The play of the valves will be clear from their positions. The piston pump has its packing in the piston itself, while in the plunger pump the packing is in a stationary stuffing box forming part of the casing.

In the boiler house, either piston or plunger pump is used to feed water into the boilers (feed pump); high-speed centrifugal pumps are now also used for that purpose. For forcing a muddy liquid through a filter-press, pressures of 40 to 60 pounds are often required and a triplex plunger pump is well adapted. The speed varies greatly with the kind of service performed, but in general, it is rather low, 30 to 60 double strokes per minute.

In the **diaphragm pump** the liquid to be moved does not come in contact with the pumping element. An example of this type of pump is the Dorrco.

Rotary Pumps with Direct Action. The gear pump, shown in Figure 217, carries the liquid between the casing and the teeth of the gears. The friction is considerable, and the gear pump is therefore chiefly used for oil and other liquids which have lubricating properties. The size is nearly always small, and the capacity of the pump correspondingly small; its simplicity and reliability have led to its general use for such purposes as pumping fuel oil to the burner.

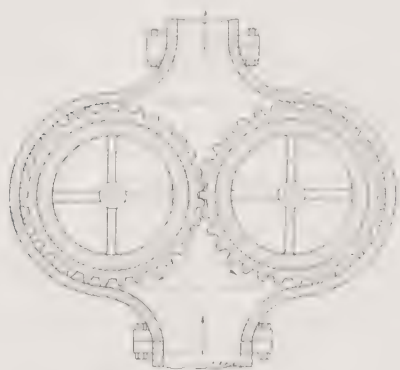


FIGURE 217.—A gear pump.



FIGURE 218.—A sliding vane pump, of the ring type.

In the **sliding vane pump**, (Fig. 218) the rotor and shaft are eccentric to the casing; the rotor carries each slide in and out because they rest on a stationary ring which is centered; the casing itself is circular. This type of sliding vane pump is the ring type¹; its operation will be clear from the sketch. There are many other modifications of this pump; in the earlier models, the casing was elliptical. The sliding vane pump has again no valve in the strict sense; it has wide passages, so that it is well adapted for slurries, and for liquids carrying lumps of soft solids. The sizes are rather small; the suction line varies from 1 to 4 inches, although larger sizes may be built and operated with fair efficiency. The pump with 4-inch suction line and 4-inch discharge line has a capacity of 200 gallons per minute at a speed of 150 r.p.m.

In the **two-vane pump**, the action is the same as in the gear pump; the water is pushed between the casing and the vane; the operation is indicated in the four-stage figure adjoined (Fig. 219). Each vane shaft carries a toothed wheel, and the two wheels mesh; one shaft carries the driving pulley, which causes both to rotate against each other. Such pumps are made in

¹ Such as manufactured for example by the Taber Pump Co., of Buffalo, N. Y.

all as well as very large sizes; a capacity of 63 cubic feet per revolution will be below the maximum. The speed is moderate (up to 250 r.p.m.).

Centrifugal Pumps. A centrifugal pump is a rotary pump with indirect action. The moving element is a disk, usually vertical, rotated by a horizontal shaft; the disk carries curved blades, and is contained in a spiral casing with close-fitting side walls. The water enters through an opening at the center of the disk, and the water is caught in the channels between the blades; the latter do not quite reach the central part of the disk. The water is delivered to the gradually widening spiral part of the casing; it acquires a high velocity from the rapidly rotating wheel, and passes out of

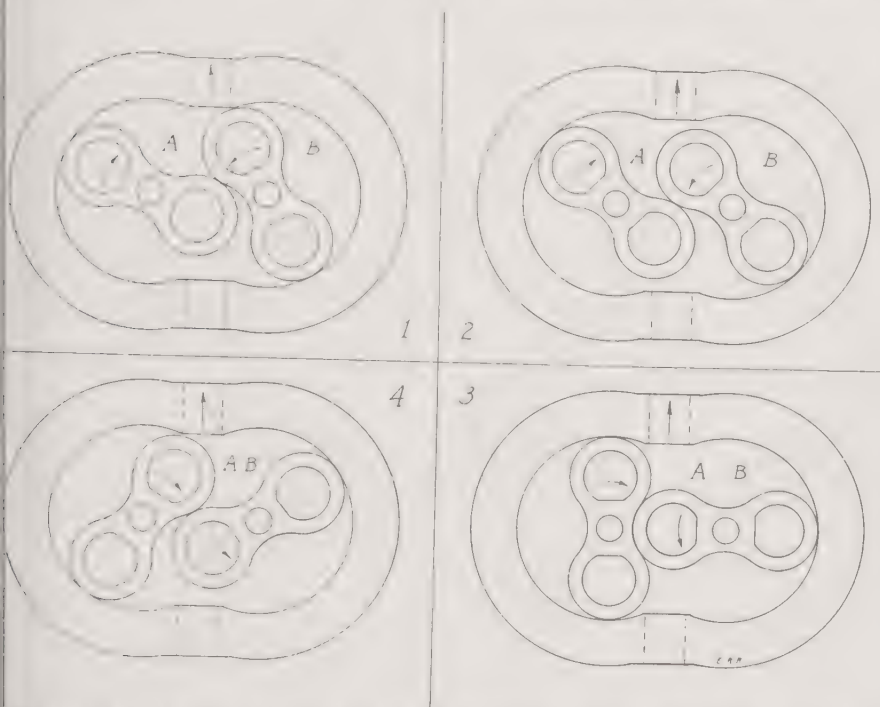


FIGURE 219.—Four stages in one-third of a revolution in a Connersville blower, of the two-impeller type; Stage 1, volume *B* is ready to be discharged; Stage 2, *A* and *B* are a maximum, *B* is beginning to pass to delivery outlet; Stage 3, *A* and *B* smaller than in 2; Stage 4, *A* and *B* a minimum; the difference between *A* and *B* in Stages 1 and 4 has been discharged.

passing to the discharge line with essentially the same velocity. Figure 219 is a sketch of a simple, open-impeller type centrifugal pump, single-stage. In the two- and more-stage pump, the discharge of the first stage becomes the feed of the second.

Low-pressure, single-stage centrifugal pumps are employed with satisfactory efficiency, equal to that of piston pumps, for lifts of 30 to 50 feet (Fig. 219); the efficiency usually given is 50 to 60 per cent. For lower lifts, efficiency is higher; for lifts of 90 or 100 feet, the consumption of power becomes enormous and the efficiency correspondingly low. The speed of the centrifugal pump is comparatively high; 1200 r.p.m. is a frequent speed, and

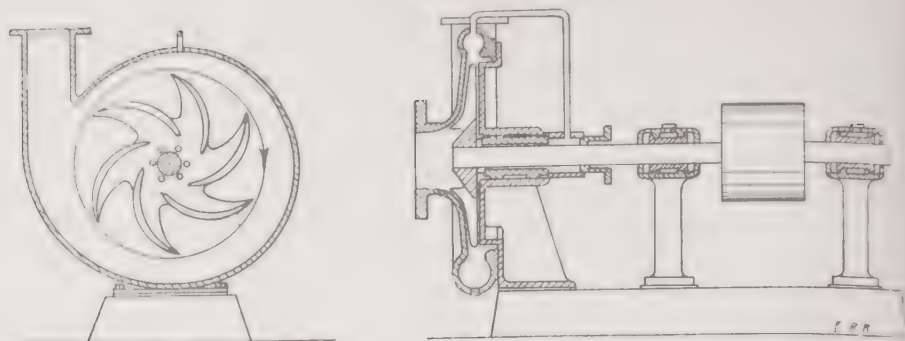


FIGURE 220.—A centrifugal pump, single-stage, open-impeller type.

1800 not uncommon. The impeller shaft is direct-connected to an electric motor shaft, or belt-driven. The direct-connected pump with its motor forms a compact pumping unit which has come into high favor; it occupies very little floor space, and operates so noiselessly that from a short distance it is impossible to tell whether it is in operation or not. All remarks in this paragraph apply to a single-stage pump; the multiple-stage pump produces higher heads with satisfactory efficiency. For viscous liquids, the centrifugal pump is useless. In giving the heads on the discharge side of the pump, it is assumed that the water floods the pump. If the water enters under a head of 15 feet the pump will raise the discharge water that much higher.

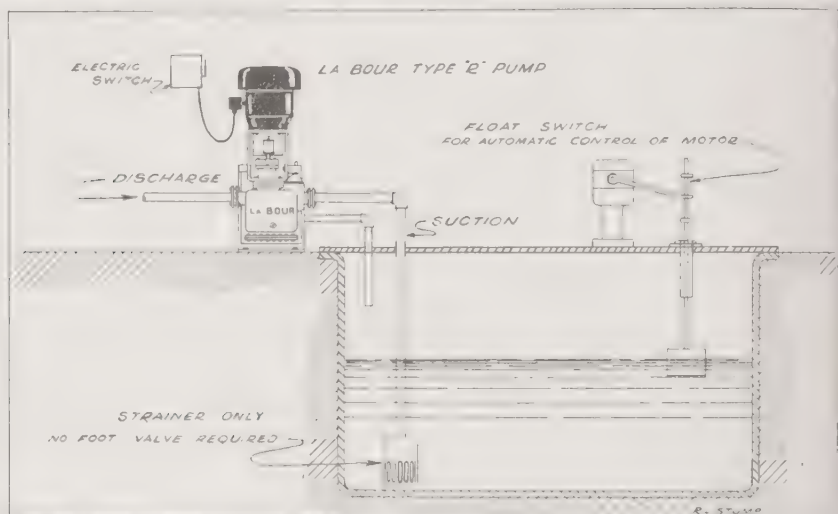


FIGURE 221.—The LaBour, type R, vertical self-priming centrifugal pump applied to sump service. The pump may be controlled by automatic float switch. No foot valve is required in the suction line. (The LaBour Pump Company, Inc., Elkhart, Indiana.)

The LaBour pump shown in Figure 221 is the most recent member of a long line of pumps which have served the chemical industries; it is a self-priming centrifugal pump, with vertical impeller.

If the water to be pumped must be drawn up from a lower elevation, the centrifugal pump must be primed, that is filled with water, and the water in the suction line also, before it can pump. The suction lift must not be over 28

for any type of pump, piston pump included. It may be noted also that the centrifugal pump has no valve, hence is adapted to muddy liquids. Next in complexity to the open impeller is the closed impeller, usually a torus, consisting of two disks separated by the curved blades which act on the water; the casing is close-fitting on both sides of the double disk. The variety in construction is very great. In size centrifugal pumps are made with 20-inch suction line and smaller; in industrial plants, the 3- and 4-inch suction line is the general practice.

For certain purposes, such as fire pumps and boiler-feed pumps, centrifugal pumps are used which are driven at speeds varying between 3000 and 20,000 r.p.m. and even more; for such speeds, it is general to use the steam turbine as the driving mechanism.

The centrifugal pump may be considered a water turbine reversed; instead of a flow of water driving the shaft of the generator, it is the generator shaft which rotates the water wheel and drives the water in the opposite direction (Chapter 12).

FANS, BLOWERS, EXHAUSTERS, AND COMPRESSORS

For the propulsion of air and gases, fans, blowers, and exhausters are employed. A fan moves a great volume of air (or gas) at slight pressure; for instance it may take the exhaust gases from a blast furnace and deliver them to the base of a tall stack. The word "fan" covers both blowers and exhausters: a blower takes fresh air from the outside and delivers it to a desired point; an exhauster takes foul air from a certain room and delivers it to the outside air. The essential operation of the blower and exhauster is the same, but the openings in the casings differ.

Fans are volume blowers; compressors are pressure blowers. The compressor delivers a small quantity of air at a high pressure; between the two extremes there are machines which deliver considerable volumes at appropriate pressures, for example 3550 cubic feet per minute at the pressure of 4 inches of water. Such devices are often called pressure blowers, but they may be classified as low-pressure compressors. A fan of medium size would be one which delivers 11,400 cubic feet of gas per minute against a pressure of one-fourth inch of water.

A fan may have 6 or 8 flat steel blades, or in a different type, 60 very thin curved blades; the latter would belong to the multi-bladed type.

Compressors furnish air or gas at a high pressure, compared to the pressure against which a fan works. The low-pressure compressor described here works against a pressure of less than one pound; it is a single-stage machine, and such single-stage compressors are suitable for pressures up to 50 pounds. For pressures between 50 and 500 pounds, double-stage compressors are used, with an intermediate cooler. For pressures between 500 and 1000 pounds, 3-stage compressors, and for pressures above 1000 pounds, 4-stage compressors are used, with cooling between stages. A single-stage compression to a very high pressure is not practical²; the heat developed is so great that on cooling in the conduits, a much lower pressure would be obtained. The heat on compressing must therefore be removed, and the cold

²The compression curve is too near the adiabatic curve and too far from the isothermal curve.

compressed gas, at 50 pounds for example, may then be compressed a second time.

Fans are generally belt-driven, usually from a special motor. Low-pressure compressors are also belt-driven; high-pressure compressors are direct-connected to steam pistons, or to motors.

Multi-bladed Fans. A multi-bladed fan, the Sirocco,³ is shown in Figure 222. The volume of air moved by the fan depends upon the speed of the wheel and upon the pressure. The higher the pressure against which the fan discharges, the lower the volume discharged; the lower the speed of the wheel, the lower the discharge. Furthermore, the lower the pressure of the air entering the fan, the lower the volume discharged.

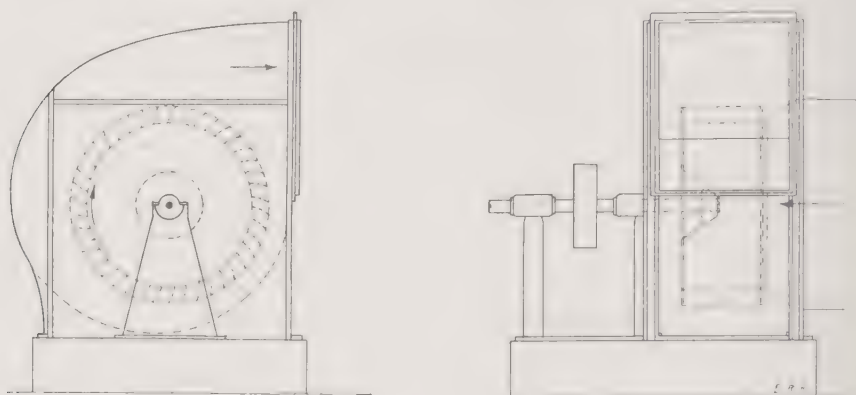


FIGURE 222.—A multi-bladed fan.

The capacity of any fan or compressor is computed on the basis of free air, that is, air at atmospheric pressure and at 60° F. (15° C.); if the gas moved is at an elevated temperature, the volume moved, computed to its true volume at 60° F., will be less than if it had been cold. All these factors are taken into consideration in the tables of capacities which the manufacturers supply on request.

Compressors. A low-pressure compressor used extensively in the chemical industries is the Connersville blower, of the same construction as the two-vane pump described in the first part of the chapter. The Connersville blower gives pressures varying from a fraction of a pound to eight pounds per square inch. It is manufactured in all sizes. A medium size would be the 13-foot capacity compressor, which, run at 350 r.p.m., furnishes 4550 cubic feet (calculated) per minute, actually 3640 cubic feet; the difference is due to a slip between the casing and the vane and between the two vanes.

The Nash Hytor is also a low-pressure compressor, furnishing air under pressures of the same range as the Connersville. Its construction and operation will be clear from Figure 223. The elliptical casing contains water which alternately leaves the rotor, and fills it. The air is carried in the buckets formed by the vanes and the liquid, from the inlet A to the outlet B. The small sizes for 50 cubic feet of free air per minute (against 10-pound pressure) have a speed of 1600 r.p.m.; the large size, for 2250 cubic feet dis-

³ Made by the American Blower Company, of Detroit, Mich.

large against the same pressure, has a speed of 230 r.p.m. The Nash Hytor may be built of special metal, and is used with concentrated sulfuric acid as working fluid for the compression of chlorine gas (Chapter 5).

High-pressure compressors resemble piston pumps, except that the valves are feather valves as a rule. The feather valve (Laidlaw) is a thin, steel plate, held against the shoulders of a port by a suitable frame. It lifts from the seat one-thirty-second of an inch, or similar distances,

FIGURE 223.—The Nash Hytor (compressor). *A* and *C* are inlet ports, *B* and *D* outlet ports. The cross-hatched areas represent the gas volume being moved, the clear area within the casing, the liquid employed.



which are sufficient to allow the compressed air to pass to the other side of the valve. Cooling between stages is by means of tubes laid in cold water. The development of the direct synthesis of ammonia from atmospheric nitrogen and hydrogen has greatly stimulated the design of high-pressure compression.

VALVES AND PULLEYS

For water lines and for liquids in general, the slot or gate valve is used. Especially if the liquid is not under pressure. For steam lines the globe valve is employed; it has a pressure side and a discharge side, and is so designed that the pressure of the steam (also water) is exerted on the under side of the movable disk. In addition to these two, the chemical engineer has utilized the plug valve, operated from a threaded stem above, or from a handle with joint below the bottom of a tank. The plug valve has the advantage that, when it is opened, the passages for the liquor or slurry are wide and not easily obstructed. Plug valves are frequently home-made. For gases, valves, cocks are used in water and steam lines.

A pump may be driven by a belt which receives its motion from the shaft of a motor; in that case the motor pulley is the driving pulley; the pump pulley, the driven. The number of revolutions per minute of the two pulleys is inversely proportional to their diameters or their circumferences. For pumps driven by gears the relation of the revolutions per minute is inversely proportional to the relation of the number of teeth on the pinion (small wheel) and gear (large wheel).

OTHER PATENTS

149,557, high pressure centrifugal pump of low capacity and economical operation; 127, a centrifugal pump, especially adapted for pumping more or less viscous liquids or fluids such as sewage sludge; 1,863,160, rotary pump consisting of two meshing gears; 1,887,873, centrifugal fan, of the propeller type; 1,884,067, a fan

for pneumatic blowers; 1,821,484, spiral blade fan, designed especially for use in connection with air-cooled engines; 1,778,041, vertical blower of the propeller type, with convergent-divergent casing; 1,787,062, multiblade blower; 1,853,973, centrifugal compressor or blower; 1,854,692, compressor and vacuum pump for air and other gases which has a rotary member which is eccentrically mounted within a cylinder and provided with blades movably mounted in slots and which engage the inner face of the cylinder, thereby forming pockets within which the air is gradually compressed as the rotor turns, due to the progressively decreasing volume of the space between it and the wall of the cylinder; 1,816,403, high-pressure reciprocating piston compressor; 1,867,651, hydroair compressor and vacuum pump (rotary pump having a series of buckets).

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*the task of separating a solid from the liquid in which it is suspended
its itself in nearly every chemical plant; this task can be discharged
usually only if the plant chemist is acquainted with all types of devices
le for such separations.*

Chapter 42

Appliances Used by the Chemical Engineer II. Filters

The separation of comparatively small amounts of solids from larger
amounts of liquids is done by settling, followed by decantation of the super-
natant clear liquid, or by the use of a filtering device. The separation of
small amounts of liquids from large amounts of solids is done by drain-
ing or by centrifuging.

Settling out the solid is the cheapest method, and is frequently used. If
the operation is extensive, a large capacity in settling tanks is required;
they act also as storage tanks. If the liquor is hot, the tank may be
supported by strips of wood. As a rule, this process is too slow; also, the
liquid collected in the bottom of the tank still contains too much water, and
must usually be sent through a filter, a combination of settling and filtering.

Filtering devices include gravity filters, pressure filters, more commonly
filter-presses, and suction filters. Several points must be considered
in studying a filtration problem: whether the cake or the filtrate is the
desired part, whether or not washing is required, and whether the operation
is to be continuous or intermittent. These considerations will have weight
in the choice of the device. Other considerations are capacity, first cost, and
operating cost, which includes repair costs and, more important, operating

At the end of the chapter, these points will be reviewed.

A suspension to be filtered is called a slurry, if its content in solids is
so high that it does not flow and cannot be pumped; slurries contain
less than 1 per cent to 40 per cent of solids, by weight. Suspensions
containing more than 40 per cent of solids are more properly called sludges.
The solid separated in the filter device is called the cake, the clear liquor
that runs off is the filtrate. Filtering devices such as filter-presses and suction
filters are really frames for the support of the filtering medium, the filter
which may be cotton duck of various thicknesses, muslin, paper,
cloth, funnel, or metal wire woven into cloth, such as iron wire, nickel wire,
or monel wire.

Gravity Filter. In the gravity filter, the slurry lies over a bed of
inert pebbles, for instance, with channels between the larger pebbles
to permit escape of the clear liquor. The mud is deposited on the sand; the
clear liquor passes through by the action of gravity. The most extensive use of
the gravity filter is made in the filtration of drinking water on a large scale
(see Fig. 13).

A filter paper in a glass or porcelain funnel is a gravity filter; it is used
extensively in the chemical industry for manufacturing reagents and certain rare
chemicals.

The Pressure Filters, Plate-and-Frame Type. The most familiar filter press is the plate-and-frame press; it consists of separate cast-iron square pieces, the plates proper, and the frames, which rest on two horizontal bars, and which may be squeezed together by a movable end-piece work against a fixed front end. The surfaces which touch are machined, so that the fit is perfect. Each frame is covered by a filter cloth which extends over all of it, and on both sides; when the press is closed, the edges of the cloth form the gaskets between the machined surfaces. The cloths are provided with small openings to correspond to the eyes in each plate and frame; the closed press these eyes form a conduit on one side for the slurry, and on the other side, for the entering wash water. In Figure 224 three pieces are shown: a non-washable plate, a frame, and a washable plate. The openings marked *A* form the slurry line; the only port in this line is to the frame. The openings marked *B* form the wash-water inlet line; its only port is to the washable plate, on the right. The non-washable plate has no ports. When filtering, both kinds of plates deliver the clear liquor at the outlet; the slurry enters in the frame, and its liquor passes through the filter cloth in order to reach the channels in the plates. As a rule washing must be done; if

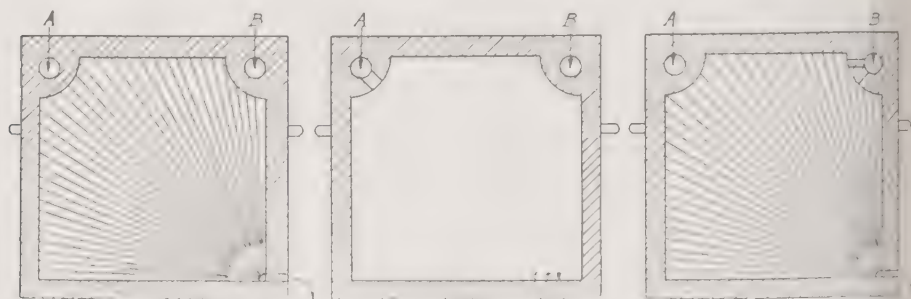


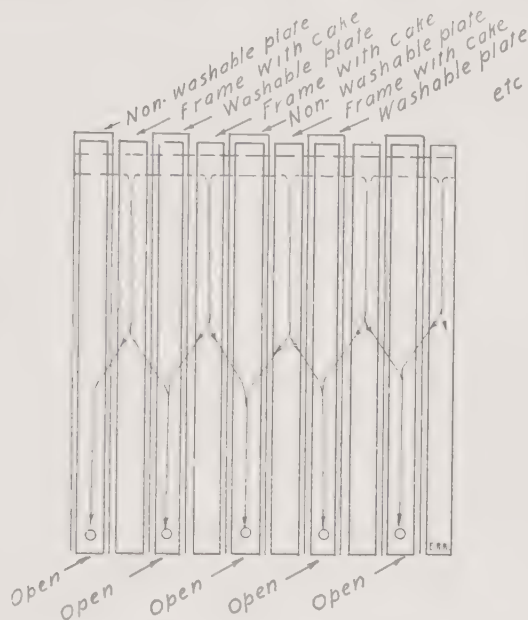
FIGURE 224.—Plates and frame for a filter press: to the left, a non-washable plate; in the center, a frame; to the right, a washable plate; the eyes at *A* form the slurry line, open only to the frame; the eyes at *B* form the wash-water line, open only to the washable plate.

liquid is the valuable part, none must be left in the cake; if the solid is the valuable part, the adhering liquid carries impurities which must be removed. When washing, the outlet of the washable plate, at the right, is closed; the one in the non-washable plate remains open. The wash must now pass through a cloth, through the cake, and through another cloth before it reaches the channels in the non-washable plate and from these, the outlet. The arrangements for filtering and for washing are shown in the two front views of five plates and five frames each.

Slurry is fed to the press until the frame is completely filled with cake; at this point, the pressure in the slurry line increases beyond the usual limit, and at the same time, the amount of filtrate decreases. The washing will be imperfectly done unless every frame is filled with cake. As the first liquor passes through the cloth, it is turbid, and is run to an intermediate receiver from which it is sent to the filter again; the reason for this turbidity is that the filtering is done not by the cloths themselves, but by a thin layer of mud which coats them in the first few moments. After a few minutes

is clear. If the solids are low, it may take 12 hours to fill the frames with mud; two hours is nearer the average time; the difference is due to the percentage of solids in the slurry, and to the size of the frames. When these are filled, the liquor line is closed, and the wash water is admitted through the bottom; the washing may be followed by testing the density of the liquid with a hydrometer; it is continued as far as the conditions warrant. If the solids are insoluble, and the wash water may be run to the sewer; washing is continued until the water removes nothing more from the cake. If the solids are valueless, only so much wash should be collected as can be reused in the process without concentration, for only when the material is expensive

FIGURE 225.—Five plates and five frames when filtering.



bear the cost of fuel for the concentration of weak wash waters. After washing is carried to the desired point, the press is opened, the plates are pushed apart and the cake in the frames dumped into a hopper or floor, which leads to barrows, or carts, or a screw conveyor. The plates are pushed together again, the press closed, and it is then ready for the next filling.

At the head of a cart, the valueless cake may be flushed away without labor by running the chute to a tank with a stirrer, and feeding a strong flow of water with continuous overflow of muddy water to the sewer.

When washing of the cake requires that it be not too high in solubles, for the solubles to dissolve, the cake is weakened, and "rots"; as soon as one channel is formed all the water will flow through that, and there will be no washing. For this reason, a different procedure is sometimes used. A first filtering removes the liquor, leaving a "strong" cake, which is not washed in the press. Instead, it is dumped into a tank with stirrer, and there it is washed with wash water from a later operation; the solubles are now

well dissolved, and this slurry is filter-pressed in its turn, and this time it is washed; the "weak" cake is so low in solubles that it will not rot.

A press with twelve plates and twelve frames each 12 inches square is a small press; one with 350 circular plates, 5 feet in diameter, is an unusually large one. In ordinary plant work, a press with 49 plates, each 3 feet square, and 50 frames 2 inches thick, is usual; such a press, fed with 1 per cent slurry, whose solids are low in soluble salts, will have a cycle of $2\frac{1}{2}$ hours; three-quarters hour to fill; one-half hour to wash, $1\frac{1}{4}$ hours to dump and close; it will dump 4000 pounds of mud. This figure will vary with the density of the cake, and with other conditions; it is given to indicate the duration and extent of such operations.

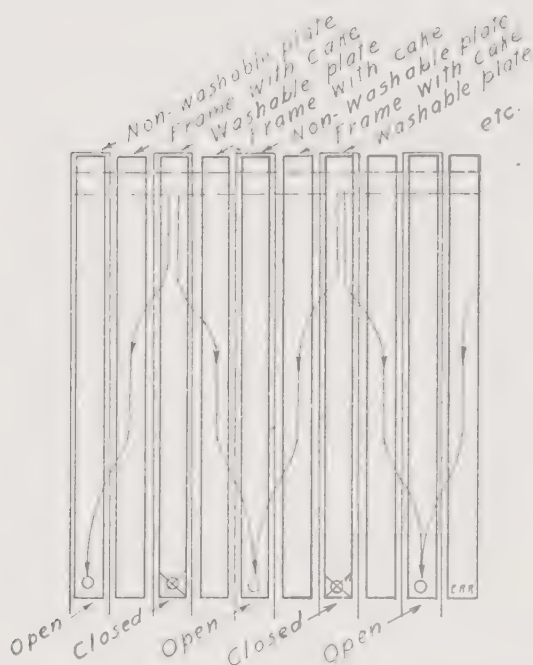


FIGURE 226.—Five plates and five frames when washing.

Cast-iron is the most common material, but wood is frequently required; other materials rarely. As indicated before, the plates may be circular as well as square. The frames may be thicker, 4 inches for example, so that they will hold more cake; 2-inch thickness is rarely exceeded if washing must be done. The plate and frame may be combined in one, giving the so-called recessed plate; many other modifications are on the market. Presses are usually opened and closed by hand, by means of a long bar turning the terminal screw which actuates the movable end piece; for very large sizes, mechanical power is used.

The slurry is forced into the pump by means of a duplex pressure pump, or a triplex plunger pump, or a blowcase whose principle of operation is similar to that of the acid egg. The pressure varies from 3 to 40 pounds at the start to as high as 40 pounds when the press is full.

The Shell-and-Leaves Type of Press. In this type of press, light frames bearing the filter cloths are provided, which fit in a steel shell.

filtration, the slurry fills the shell, entirely surrounding the cloths; become coated by the cake, while the clear liquor reaches the inside of frames and runs off through a pipe connection at the base. In the press, one of the most successful representatives of this class, the



FIGURE 227.—Longitudinal cross-section of a 48 by 120-inch Kelly press, showing filter leaves and slurry inlet at *E*.



FIGURE 228.—Front view of the Kelly press, with one-half of the movable head plate removed to show the filter leaves.

are rectangular, and are fastened to the cast-iron head; the shell is circular, lying on its side. The leaves and cast-iron head are mounted on a carriage having four small wheels, which run on two rails set inside the head and on the outside extension of the rails. After the desired thickness of cake has formed, the carriage is pulled out horizontally by chains actuated by a small compressed air motor, and the cake is dumped by jarring the leaves with a long pole, aided by a stream of water from a hose. After the cake is dumped, the motor is started in reverse, the carriage is pulled in,

FIGURE 229.—Cross-section of a filtering leaf in the Kelly press, with cake on both sides, ready to be dumped.



the press closes. The construction is made clearer by the three illustrations adjoined (Figs. 227, 228, 229).

The main advantage of the Kelly press is the ease in dumping; the cake hangs onto the frames and is easily dislodged; the amount of hand labor is low. The slurry enters near the center of the shell at its base.

from a blowcase located on a lower floor; the filtrate runs out through cocks in the head of the press into a trough which delivers it to a dividing box set at the side, out of the way of the pulled-out carriage. On closing the chains pull through a toggle joint which forces the head tightly in place and lock it by pushing stout steel bolts into the receiving hoops in the shell.

If the cake must be washed, the slurry remaining in the shell after complete cake formation is run back into the blowcase, and water introduced. The progress of the washing is followed as it is in the plate and frame press.

Because of the ease of dumping, the cycle for the Kelly is short, and its capacity per day is high. A press 48 inches in diameter and 120 inches long will dump 4000 pounds of washed cake in $1\frac{1}{2}$ hours, distributed as follows: three-fourths hour to build the cake, one-half hour to wash, and one-fourth hour to open, dump, and close the press. These values will vary widely with the percentage solids in the slurry, and with the permeability to water of the cake, and its density. The merits and defects of this press will be discussed after the third type, the automatic continuous suction filter, has been described.

The Sweetland press is another example of the shell-and-leaves type. In the Sweetland, the leaves are stationary, and the shell, which is divided in two halves horizontally, hinged together, opens jaw-like to allow the cake to be dumped.

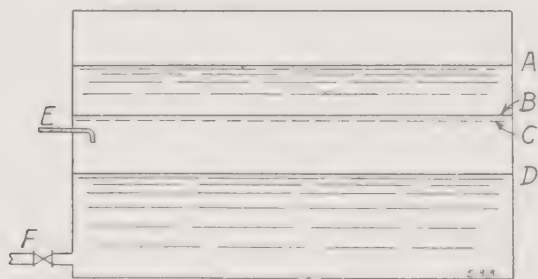


FIGURE 230.—Stationary suction filter; A, level of the slurry; B, filter cloth; C, false bottom; D, level of the clear filtrate; E, suction pump connection; F, liquor outlet.

The Stationary Suction Filter. The simplest type of suction filter consists of a two-compartment box, usually circular; a perforated plate on which the filter cloth is spread separates the two compartments. The slurry is run on top of the cloth; the lower compartment box has two connections: the upper one for a suction pump, the lower one for running off the liquor. When the suction pump is connected and the clear liquid passes into the lower compartment. When this is nearly full the suction is disconnected, and the filtrate run off through the lower connection. Usually the size is so proportioned that a batch of slurry may be filtered without interruption. Stationary suction filters of this type are constructed of lead, stoneware, or cast iron, and have been made as large as 6 feet in diameter. They give good service for slurries with a low percentage of coarse solids, such as a ferric sulfate liquor containing some suspended sulfur. "Nutsch" is an old name for the stationary suction filter and is gradually going out of use in America.

The operation is intermittent; the liquor could be removed continuously by drawing it off as fast as it collects, through a separator, to which

a pump would be connected; the liquor would drop out into the closed filter. But this would not provide for the removal of the cake on the filter. A shutdown every little while would be necessary in order to remove the more solid the slurry contains, the more frequent the interruption. Difficulty is removed in the rotary suction filter.

Another way to employ suction for filtration with intermittent operation is using *filter leaves*, suspended in the slurry with suitable connections for suction. The liquid passes through the covering cloth, while the mud coats the sides of the leaves. After this coating has reached a certain thickness the leaves are lifted out by a traveling hoist or an overhead crane and dumped into a wash tank or re-slurry tank. The Moore filter leaves are so used at the Freeport plant (Texas) for collecting magnesium hydroxide from water.¹

The Rotary Suction Filter, Drum Type. The rotary suction filter is automatic, and has continuous cake discharge, continuous filtration and continuous discharge. One of the well-known examples of this type is the Oliver, which consists of a cylinder or drum lying on its side and carrying the filter cloth, of a

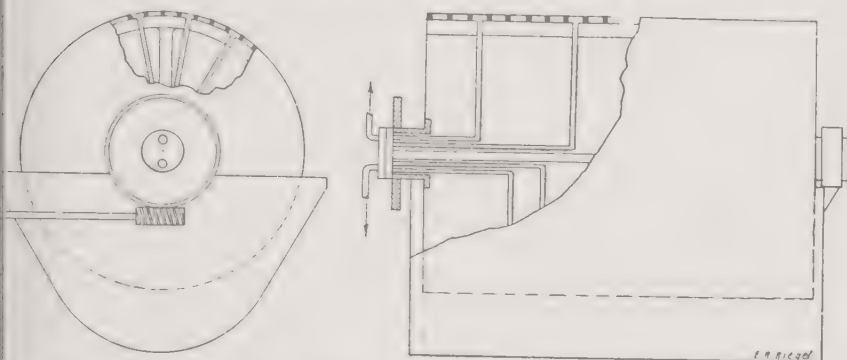


FIGURE 231.—The Oliver continuous suction filter; front and side view.

scraper for the discharge of the cake, of a tank holding the slurry, and auxiliary apparatus such as pumps and receivers. The drum is mounted on a horizontal shaft carried by the slurry tank, and dips into the slurry to a depth shown in Figure 232; liquor is drawn in, and the surface is coated with cake; as the drum revolves the cake emerges and meets with water which is applied by a spray; as it revolves further, the cake meets the discharge knife. At the moment the cloth nears the knife steam under pressure forces it out slightly, bulging it, causing clearing and clearing the meshes. The knife does not bear on the cloth, as it would wear it too fast, but on a wire wound over the cloth, spaced one inch apart or so.

The simultaneous application of suction for the filtrate, suction for the water, and steam (or compressed air) for the blow is achieved by means of an ingenious mechanism, the circular valve. It consists of two concentric circles, one of which rotates with the drum, while the other is held stationary. The liquor lines; a stud set in the rotating half bears on a spring with

loose collar which forces the stationary half tightly against the rotating half. The location of the valve is at the end of the shaft as shown in the illustrations. The surface of the drum consists of shallow wooden or iron chambers 12 inches square, covered with sections of one-fourth-inch wire netting to support the cloth. Each chamber has a pipe connecting the valve, running first radially to the shaft, and from there through a connection which unites the liquor from all sections lying along a horizontal line to a port in the rotating half of the valve. These ports form a circle in the stationary half of the valve has a circular channel fitting over this circle. The channel may be divided into compartments by means of small bridges (if the valve is brass). One such compartment would form the clear

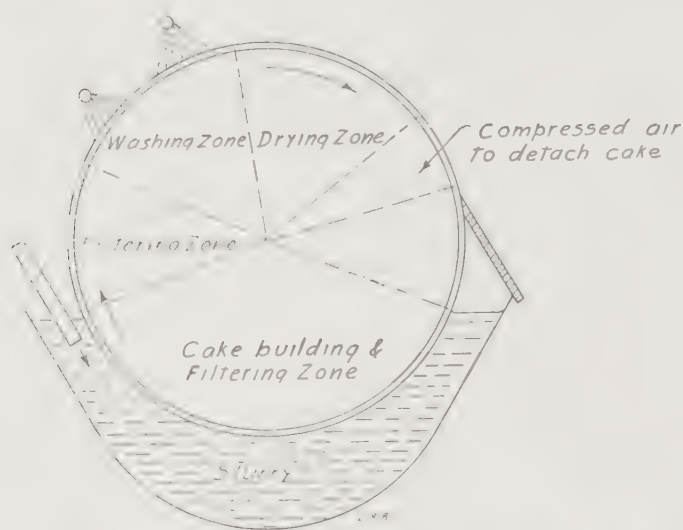


FIGURE 232. — Filter drum of the Olive continuous suction filter, showing the filtering, washing, drying, and blowing zones.

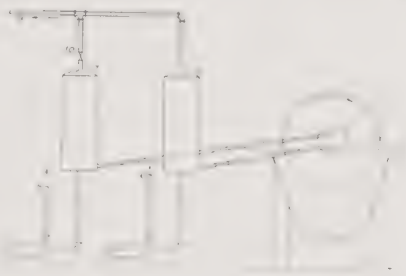
liquor compartment and communicate with the clear liquor line, there would be the wash-water compartment, feeding the wash-water line; a very small compartment, fitting one port only, would bring the steam blow. Since the bridges are movable, the number of ports in connection with the clear liquor line may be varied; if increased, for instance, it would have the effect of bringing more drum surface under the action of the clear liquor. If at the same time the submergence of the drum is increased, which may be readily done by raising the level of the slurry in the slurry tank, it would mean a greater zone for cake building. The proper adjustment of the stationary half of the valve is made through a special valve rod.

The valve surfaces are machine-faced to give perfect surfaces; they are lubricated from two or more pressure grease cups; the wear is slight because the drum revolves once in 7 minutes, or similar speeds. Each port fits perfectly against the inset bridges, so that no internal leaks can take place. For alkaline liquors, the valve should be of cast iron.

A suction pump pulls out the liquor and any false air which has been taken in, to a separator, wherein the liquor drops to the bottom and is pumped out by a separate liquor pump, while the air rises and is removed by another suction pump. The same suction pump serves for the wash water, and

is reduced by means of a reducing valve, for it is well that the cake be pulled in rapidly, but a definite period of time should be provided in which the wash water may remain in contact with the cake. The cake is pulled through a separator, from which the wash liquor is pulled out by means of a separate pump. A complete assembly is shown in Figure 233. The cake is discharged by the knife onto an apron, and from there may be moved by a screw conveyor. The feed of the slurry to the tank, the turning off of the clear filtrate, the application and removal of the wash water, and the discharge of the cake are simultaneous and continuous functions. If the cake is removed automatically, the filter is automatic; no labor of any kind is required. It has considerable flexibility, so that it may be adapted to a great variation of slurries. If the percentage of solids is high,

FIGURE 233.—Assembly for a small-scale automatic vacuum suction filter; 1, filtering drum; 2, filter valve; 3, discharge knife; 4, slurry tank; 5, separator for filtrate; 6, liquor pump for filtrate; 7, separator for wash; 8, liquor pump for wash; 9, to suction pump; 10, valve for reducing suction on the wash area.



the drum revolves fast; if the percentage is low, the drum is made to revolve slowly. If no washing is needed, the submergence may be great; if washing is required, the wash zone is extended. The filter cloth is chosen from the variety of material for maximum service. It is no wonder that the automatic continuous suction filter has been very successful.

The main limitation is that of pressure, since the atmospheric pressure, 14.7 pounds, is the maximum, and all of it is rarely applied. With volatile liquids which must be filtered hot, this type of filter fails, for the solvents vaporize, and no liquid at all, in the worst cases, can be pulled through the filter. The difficulty is overcome by placing the filter inside a cylindrical pressure chamber. With concentrated, warm salt solution in water, the filter functions well, if the temperature is not over 70° to 75° C.

Dorrec Filter. In the Dorrec filter, which is also a rotary suction filter in continuous operation, the sludge is contained within the drum, whose outer wall bears the filtering medium. The dewatered, washed cake is discharged into an inner trough. There is greater ease in filtration, in that the coarse particles settle out against the filtering cloth, with the finer ones only later; the plugging of the filtering cloth should be less likely. An advantage in this novel design is that the drum can run on idling

Vacuum Suction Filter, Disk Type. The American Continuous Vacuum Filter represents the disk type among the rotary suction filters. It is a rotary vacuum filter which has been established in plant practice for many years. The filtering medium covers flat disks which are mounted centrally on a horizontal shaft through which suction is applied to the under side of the

filter cloth. The assembled shaft and disks are in turn mounted upon slurry tank. The disks revolve with their lower portion in the slurry; they emerge, the cake dries and wash may be applied. At the discharge point just before entering the slurry again, small rollers remove the cake which can drop downward because at that place the slurry tank is deeply notched. The suction pipes from the various disks terminate in the rotating part of the valve, while the stationary part carries the liquor and wash lines. The valve is faced and not flat, but of the conical plug type which possesses

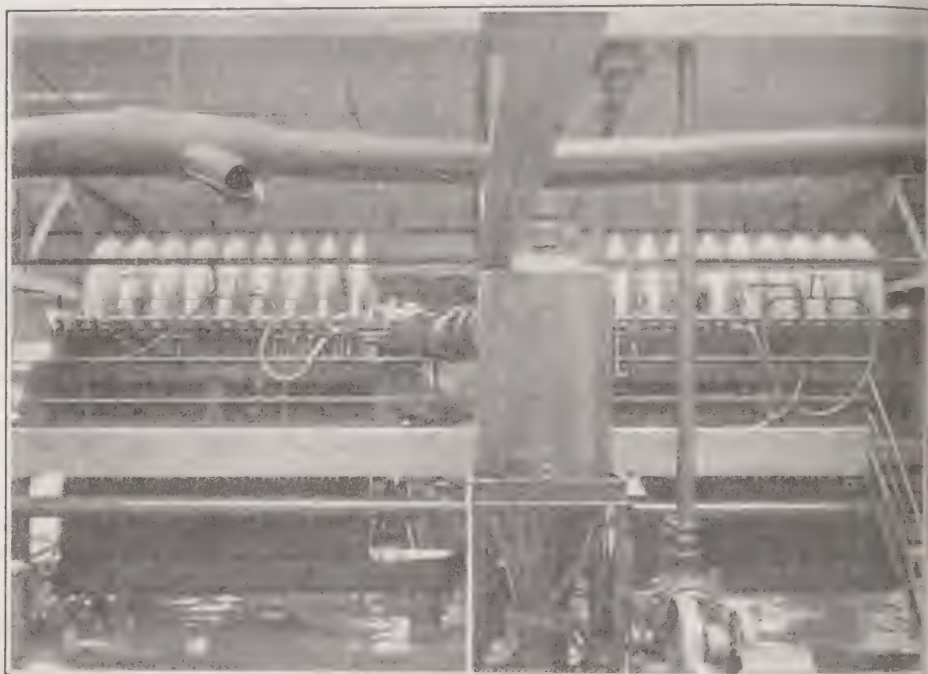


FIGURE 234.—Twin unit of an American Continuous Disk Suction Filter, showing two 9-disk units, separator and pump, as well as conveyor box on the floor of the filter cake. (Courtesy of the Oliver United Filters.)

important advantage of seating itself as a slight wear takes place. The filter requires auxiliary devices such as the drum type suction filter does—separators, suction pump and liquor pump.

The Continuous Pressure Filter. The limitation of pressure has been removed by the development of the continuous pressure filter, which resembles the suction filter, but has a casing over the drum in addition, so that pressure above atmospheric may be applied; also a closed box for the separator and a receiver for the cake must be provided. A well known example is the Vallez filter. The suction filter will continue to be used whenever possible, since it is simpler; in special cases the pressure filter must have to be substituted.

The Cuno filter is an edge filter; the dirty liquid must travel past the edges of horizontal circular plates packed close together, to reach the central outlet passage. The dirt is deposited on the upper surface of each disk

Auto filter is self-cleaning, by manual operation, and is thus adapted for continuous operation. For the removal of a small amount of suspended solids the so-called "pulp filter" or pulp filter (Kiefer) serves well. The cloudy liquid travels through thick disks of wood pulp or other masses, which retain the solids, deliver a brilliant filtrate. The beer filter is of this type. Another employs a napped blanket-like cloth, successfully applied to the filtration of syrups in the beverage industry.

Comparison of the Several Filters. On closer study, it will be found that each filter has its field which it serves better than any other; the various types supplement each other. The plate-and-frame press is the proper equipment for a process requiring one dumping a day or in several days, for then the press may be put together with care; the surfaces cleaned to give tight results. For a cake which is valuable, so that the dumping is a cautious operation, there may be several openings per day and yet this press may be the



FIGURE 235.—End view of a 24-tube unit of the oscillating continuous filter, Genter type, with valve plug exposed. The tubes extend horizontally, away from the reader. Note the 24 ports in the rotating half of the valve, and the 3 ports in the stationary half, on the floor. (Courtesy of the Bartlett Hayward Company, Baltimore, Md.)

choice. But for a valueless cake, in a press worked to capacity, opened more times per nine-hour day, the press may be closed carelessly. Usually if it is of large size. To bring the plates together, 100 plates or more will have to be pushed along the two horizontal bars; unless these are clean and well oiled, the press will not be tightly closed. Unless the plates and plates are absolutely free from grit, the surfaces will not meet and there will be a leak; even if the leaking liquor is recovered, and sent

back to the press, it is a waste of filtering capacity. Every joint between plate and frame is a potential leak, hence in a 50-frame press there are 50 such possible leaks. In this respect the Kelly press is greatly superior; it has one gasket, hence only one possible leak; to keep one gasket clean is a reasonable task, and as a result, it rarely leaks. The Oliver has no possibility for leaking except in the valve, and that is easily refaced.

The plate-and-frame press has a valuable feature in that the filtrate is visible; should one plate run dirty, it may be shut off and the filtration continued with the remaining plates; the Kelly press has the same valuable feature; in the Oliver, it is missing; if there is a break in the cloth so that mud enters, there is no way of detecting the faulty place, and all the filtrate is slightly muddy. The blow of steam or compressed air cleans the cloth well, in some cases, so that the fine layer of mud must reform, and while it does, the liquor runs slightly muddy. This constitutes a fault in the Oliver which is absent in the other two filters. If a slight turbidity does not matter, the great economy of the Oliver and similar suction filters will place it first; but if absolute clarity is required, the older presses are superior.

Both Kelly and plate-and-frame presses suffer from the fact that the operation is discontinuous; in that respect the automatic suction filter and the automatic continuous pressure filter are supreme.

Strictly speaking, filtering and washing mean a separation of the insolubles from the liquor, followed by a displacement by water of the liquor adhering to the solid. A good example is the ferric hydrate and lime mud in the solution of sodium sulfate. More than that should not be required from the filter, yet frequently more is. Thus when the cake contains salts in the solid state, it will be expected that they will be dissolved during the "washing," but "rotting" of the cake will result. This will have serious results especially in the Kelly press, because its cake is unsupported, and when the structure is weakened by the removal of salts, the cake drops into the shell, clogging the inlet and otherwise interfering with smooth operation. Another slight drawback to the shell-and-leaves type press is the necessity of running back to the blowcase a shellful of slurry once the cake has reached the proper thickness, before the press can be opened.

The centrifugal basket is also a filtering device, and very successful because it is primarily a means of rapidly draining a wet solid, it is described under that head in Chapter 43.

In first cost, the plate-and-frame press is the lowest; its operating cost is the highest, but if the slurry is low in solids, requiring infrequent openings, it remains the most economical device. For the rapid handling of a cake rich in solubles which need not be washed in the press, because the mud after dumping is reslurried, the Kelly or Sweetland will give excellent service. For a mud which must be washed with so much liquor that continuous operation is desirable, the rotary automatic suction filter, either the drum type, or the disk type, is indicated.

OTHER PATENTS

U. S. Patent 1,870,485, multiplex rotary drum filter; 1,859,282, continuous filter apparatus for removing clay, fuller's earth or other fine material, from oil; 1,780,000

and filter using two filter media; L812.773, a filter for filtering suspended solids from liquids, consisting of a vertical, tapered tube filter press.

PROBLEMS

A Kelly press dumps 4000 pounds of cake once in $2\frac{1}{2}$ hours, with one man operating the press. A plate-and-frame press dumps 4000 pounds in $2\frac{1}{2}$ hours, requiring two operators. What is the figure for hours of labor on the basis of one individual (man-hours) per 1000 pounds of cake? Inspection and repair labor is left out of consideration. If the Oliver is completely automatic, what will its man-hour figure be? Make a table comparing the three values.

An Oliver filter drum 4 feet in diameter and 6 feet on the face makes 1 revolution in 6 minutes. What is the circumferential speed? In order to raise the circumferential speed by one-half, how much faster must the filter revolve? How many feet of surface has the drum?

Thirty-two thousand pounds of wet cake are dumped per 10-hour day from plate-and-frame presses. If each frame holds 80 pounds of wet cake, how many frames has each press?

Slurry carries 10 per cent of insoluble mud, on the dry basis, that is, dewatered. How many pounds of liquor form while 10,000 pounds of cake are collected on presses? If the density of the filtrate is 1.44, how many cubic feet of liquor are there? If the density was 1, it would take 62.5 pounds for 1 cubic foot. How much would the filtrate liquor stand in a circular tank 12 feet in diameter? It is noted that all the liquor is forced out of the cake and collected; this is very nearly true, realized by blowing the cake with steam.

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 "Coagulating filter aids," Richard N. Cogger and Harvey M. Merker, *Ind. Eng. Chem.*, 33, 1233 (1941).

In the course of the growth of the chemical industries, a number of appliances have been devised which are characteristic of these industries. Their application has become great enough so that engineering firms devote themselves not only to a single type, such as evaporators, but to the design of the evaporators for specific industries, for example, evaporators for beet-sugar liquors, or milk, or glucose concentration.

Chapter 43

Appliances Used by the Chemical Engineer III. Evaporators, Driers, Cottrell Precipitator, and Others

Among the appliances which have been perfected to a high degree of efficiency are the evaporators, whose heat source is usually steam; the most economical form, the triple-effect evaporator, reduces the fuel consumption to almost a third. The concentration of a dissolved salt yields a liquor which on cooling deposits crystals; these are separated from adhering mother liquor on a drain board, or more rapidly in a centrifuge. In many cases the substance must be absolutely dry, and this may be done in cabinet driers, vacuum driers, or most economically, in a rotary drier. Crystallizers and driers are important appliances.

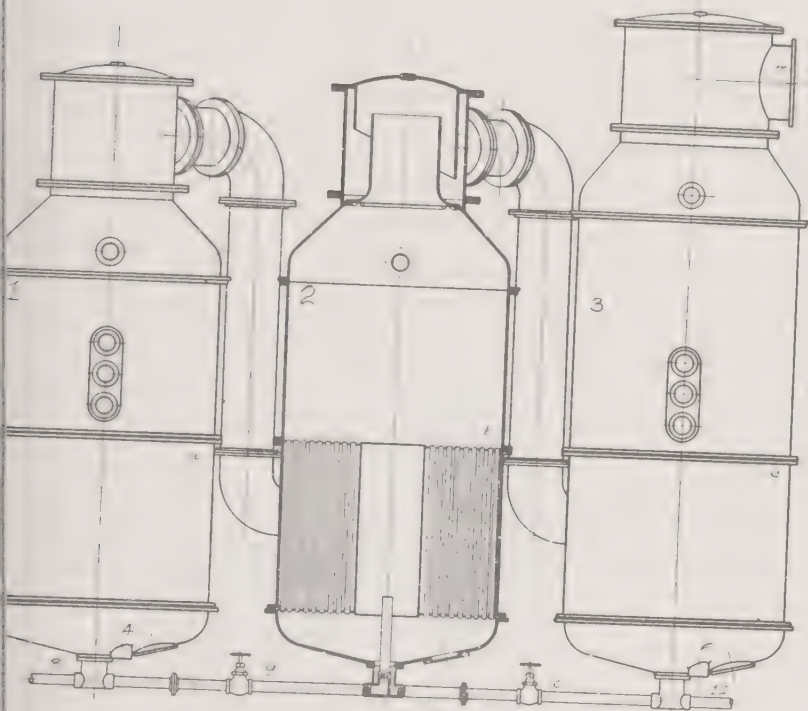
An appliance not far removed in form and in principle from the type of drier known as the drum drier is the chip machine, which permits the rapid production of many substances in the form of thin chips which possess properties making them much superior to lumps.

The dust collector, the Dorr thickener, and mixers for pasty solids are frequently indispensable.

An electrical appliance which the chemical engineer uses freely is the Cottrell precipitator for dust and mists.

Evaporators. The simplest kind of evaporator is the open kettle built over a fire, or the open pan, in the path of waste heat gases. Heating by means of steam, either in coils or in a chest with numerous horizontal or vertical tubes placed in the liquor is the usual practice; the vessel is closed except for an outlet for the steam rising from the liquor, and this outlet may be closed by a valve. The use of steam in the coils permits a close regulation of temperature, and the closed vessel allows the transfer of its contents to an elevated point by applying compressed air, on the principle of an acid egg. The single evaporator, working at atmospheric pressure, is largely used for the concentration of a solution which remains clear while in the evaporator, and deposits crystals only as it cools after transfer to the crystallizers; for such cases, the steam chest may be placed near the bottom. In the case of sodium chloride, there is a separation of the solid as the evaporation progresses, and it accumulates at the base of the vessel in the conical part provided; the salt in the cone is more or less undisturbed because the steam chest is situated well above it. For such a case, as the glycerin from a soap kettle, the concentration is performed at reduced pressure; the salt is removed at intervals without interrupting the evaporation.

lid of a salt box which is also under suction; by closing the valve at the base of the cone, the salt box can be emptied, then closed again, and refilled, when it is ready to receive another salt dump. For a number of products, the fuel item is so important that the triple-effect evaporator is used; familiar cases are the salt (NaCl) and the sugar, particularly beet sugar. The triple-effect evaporator depends on the fact that the boiling point of any liquid in a closed vessel from



Sketch of a triple-effect evaporator. Boiler steam enters steam chest *a*, at 4 for condensed water; the steam from solution in No. 1 enters steam chest *b*; the steam from No. 2 enters steam chest *c* with outlet 6; the steam from *c* via 7 to condenser. The reduced pressures are given in the text. The solution enters No. 1 at 8; after concentration, it passes from No. 1 to No. 2 at 9, and after further concentration from No. 2 to No. 3 through 10. The concentrated liquor leaves No. 3 through 11, periodically. (Courtesy of the Geo. L. Manufacturing Co., Buffalo, N. Y.)

atmospheric air has been removed is lower than in the atmosphere; furthermore, the lowering in the boiling point is roughly proportional (absolutely) to the lowering of the pressure. The normal atmospheric pressure at sea level is 29.92 inches of mercury; the vacuum in the vessels is expressed in inches of mercury which are forced upward by the pressure against the pressure in the evaporator; an absolute vacuum is expressed by a column 29.92 inches high, since then the pressure inside is nil.

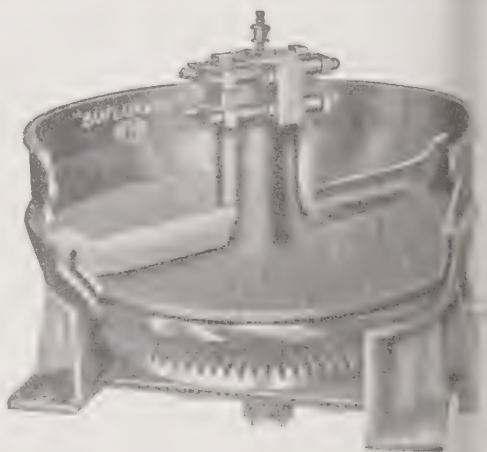
The connection between the several effects is shown in Figure 236. Vapor from the central plant enters the first steam chest and causes liquor to boil. The steam from this liquor passes to the steam chest of the second vessel, where it becomes the source of heat; after giving up its heat to the colder liquid it is liquid water, which is trapped off at the outlet of the chest. The steam arising from the liquor in the second vessel becomes the heating steam in the third chest; the water vapor rising in this vessel passes to a condenser, where cold water returns it to the liquid state. An example from the concentration of sugar solution follows¹:

	Vessel 1	Vessel 2	Vessel 3
Vacuum	2½ inches	14½ inches	26 inches
Temperature of entering steam....	220° F.	205° F.	183° F.
Temperature of boiling liquor.....	205	183	130 → condenser
Temperature fall in each vessel....	15	22	53

The same quantity of heat raises steam three times, and the saving in fuel is almost two-thirds. There is a consumption of steam running the suction pump; theoretically, it is only such as is required to pump out one vessel to the required pressure; practically, the pumping must be continued throughout the evaporation, because some air leaks in, and the liquor gives up dissolved gases, but even so, the steam consumed for the pump operation is very small, and the fuel consumption is cut nearly to one-third. There is an additional advantage in that boiling at low temperature gives a better product. Double effects and quadruple ones are also used²; more than four effects are rare.

For such an inexpensive product as salt (NaCl), the saving in fuel is most important, and triple and quadruple effects are commonly used in salt plants. They are of special construction, with conical bottom ending in a

FIGURE 237.—Jacketed crystallizer with rotating arm, for the production of small crystals. (Courtesy of Buffalo Foundry & Machine Co., Buffalo, N. Y.)



rising boot which permits constant discharge; in point of size, the evaporators for salt are probably the largest, as large as 30 feet diameter. 20-foot diameter pan is quite common, with an over-all height of 30

¹ "The manufacture of sugar from the cane and the beet," T. H. P. Heriot, New York, Green & Co., 1920, p. 259.

² An example of quadruple-effect operation will be found in *Ind. Eng. Chem.*, 10, 195 (1918).

material is usually steel, but at least one triple effect for salt is of copper lined with tin.³

For sugar solutions, the liquor in the first pan is pumped to the second where to be evaporated further; while in turn, the liquor from the second is pumped to the third pan, for still further concentration. In the plants, each effect receives brine of the same strength; the fuel saving realized in either case.

Not only solutions of solids, but of high-boiling liquids are concentrated in single- or multiple-effect evaporators. A single vessel operating under reduced pressure, and receiving, usually, highly concentrated solution from preceding evaporators, is called a vacuum pan.

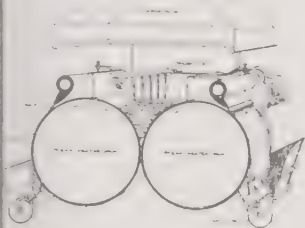


FIGURE 238.—Atmospheric double drum drier, with liquid feed. The slowly revolving hollow drums are steam heated. The dry coat is scraped off as shown; each collecting box has a screw conveyor. (Courtesy of the Buffalo Foundry & Machine Co., Buffalo, N. Y.)

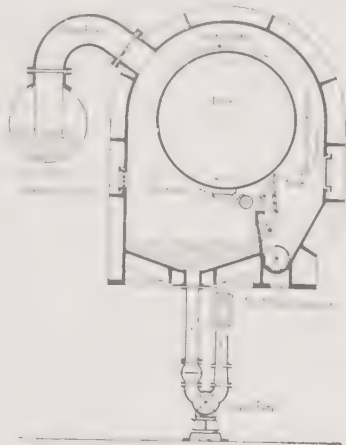


FIGURE 239.—Cross-section through a vacuum drum drier. The suction is applied to the dust collector, just behind the vapor line. The 2 boxes for the dried material not shown. The slurry is pumped to the small trough next to the spreader, and constantly overflows. (By courtesy of the Buffalo Foundry & Machine Co., Buffalo, N. Y.)

Single, double and multiple-effect evaporators are now very generally used with the heating element separate from the vapor chamber, and with vertical tubes (generally) for rapid circulation. So desirable is it in many cases to have very rapid circulation, with the resulting short period of contact with the heating tube, that a pump is provided under the vertical heating element to drive the liquid still faster through it; such devices are called as evaporators with forced circulation.

An important study of fractionating columns for the separation of mixtures by taking advantage of the differences in their vapor pressure has been treated upon in Chapters 20 and 24. In the reading references, there are found and grouped together valuable articles, which will afford the beginner a scientific study of fractionating columns.

Times Bull. No. 146, W. C. Phalen, contains numerous illustrations of multiple-effect evaporators (1920).

Crystallizers, Drain Boards, Centrifugals. The liquor from the evaporator, after suitable concentration, is blown, or pumped, to shallow vessels of steel if possible, or wood or lead-lined wood, if necessary, where it deposits its crystals on cooling. As a rule, the liquors are at rest; for the production of small crystals, a circular pan with slow agitation by a rotating arm is used, and by jacketing the pan, the temperature may be controlled. After crystallization the mother liquor is run off, and the wet crystals may be placed on a drain board which slopes toward the crystallizer; a more rapid

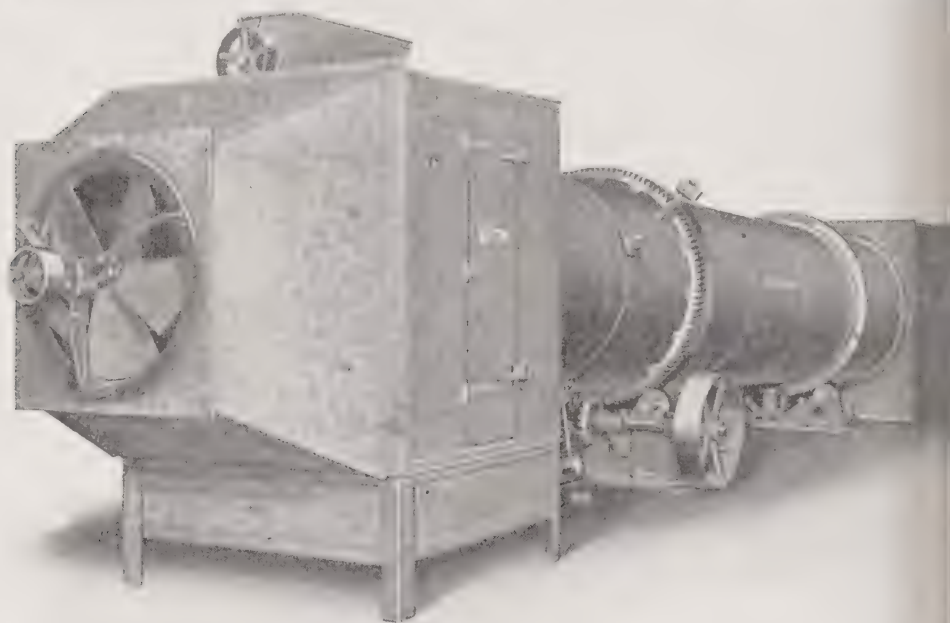


FIGURE 240. A rotary drier, from the exhaust chamber end. The fan draws air warmed over the heating coils at the other end, through the cylinder which slowly rotates. Longitudinal ribs lift the material and dump it when they reach the highest point in the rotation. The feed is at the suction end. (Courtesy of Geo. L. Squier Manufacturing Co., Buffalo, N. Y.)

of removing adhering liquor is by dumping the crystals into centrifugals, and after the proper charge has been added, setting the basket in motion. The mother liquor is whirled off and is caught in a circular apron. The modern centrifugal is driven from overhead, by direct-connected motor, and has an annular ring in the base which can be lifted for discharge through the bottom. A conveyor belt travels underneath and conveys the crystals to the screen, or drier. The continuous crystallizers consist of several connected horizontal jacketed tubes in which a scraper moves the deposited crystals forward.

Driers. Moist solids may be dried on trays placed in a closet, warmed by a few steam coils at the base. A cabinet drier is a closet with trays, and with a motor-driven fan and suitable partitions so that the air is circulated. Steam coils raise the temperature of the air to the desired point. Various driers are tray driers^{3a} in strong iron boxes which may be evacuated

^{3a} See Fig. 165.

stand on shelves which are hollow, and in which heated water, steam at various pressures, or oil heated still higher, may be circulated, so that a large range of temperature is possible.⁴ The rotary drier is gaining on all other forms, however, because of its labor-saving feature, except for small-scale operation, and for special cases. The rotary drier is a long cylinder mounted on its side, resembling the portland cement furnace, but of light construction; warmed air is pulled through the cylinder, which travels in a direction opposite to that of the solid. The latter is fed in at one end, and comes to the opposite end gradually, by virtue of a slight inclination. A rotary drier consists of a long chamber through which small cars carrying the material are slowly or periodically moved one way while warm air travels the other way. The atmospheric drum drier consists of two hollow drums revolving toward each other, and internally heated by steam; buttermilk or orange extract, for example, lies between the two drums; a thin film is car-

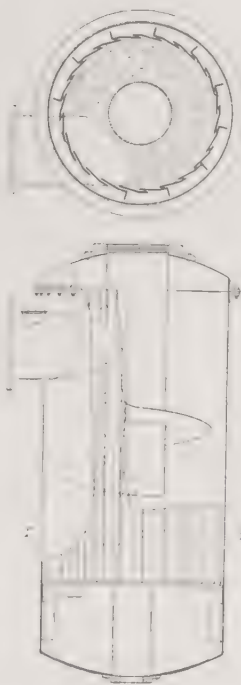


FIGURE 241.—Flick centrifugal catchall and entrainment separator. Entrained droplets pass through the slits of the inner wall, out of the path of the vapor or gas. (Courtesy of Wurster and Sanger, Inc., Chicago.)



FIGURE 242.—A dust collector.

ried by each cylinder and dries in a fraction of a revolution; a scraper scrapes the powder. The speed is slow. The drums are furnished chrome-plated, if desired; the evaporator may then be used for a number of hours which would attack iron. The same evaporation may be performed at reduced pressure by placing the drum in a housing, providing a

suction pump, a small condenser, and a conveyor with store boxes inside the evacuated area; such vacuum drum evaporators are suitable for drying dyes and for milk evaporation (copperlined).

In the Flick catchall and entrainment separator, the vapors enter tangentially, so that a circular motion is set up. (See Fig. 241.) The droplets or other suspended particles are thrown to the inner wall, and pass through its slits to the chamber between inner and outer wall, out of the path of the vapors or gas. The droplets collect and drain to a bottom discharge. The cleaned vapor leaves at the top of the separator. Such a separator is used between a single or multiple effect glycerin evaporator, for example, and the vacuum pump or ejector; any entrained liquid is recovered.

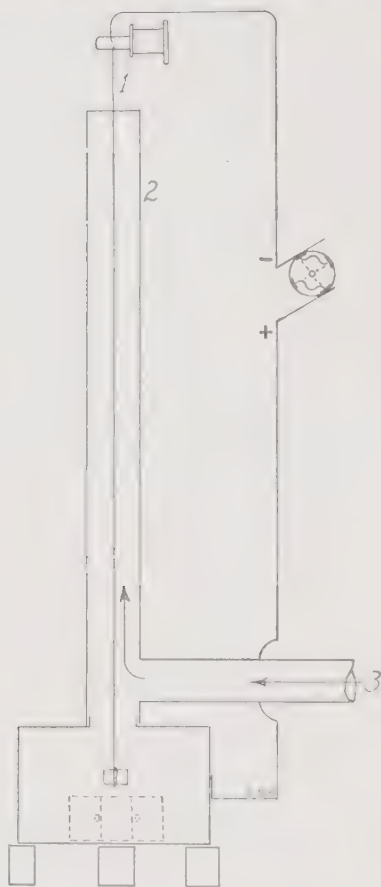


FIGURE 243.—Principle of the Cottrell electrical precipitator. The high-tension direct current passes from insulated wire 1 through the air gap, to pipe 2; the dirty gas enters at 3; clean gas issues at 1. The dirt on the pipe drops into the box below on rapping.

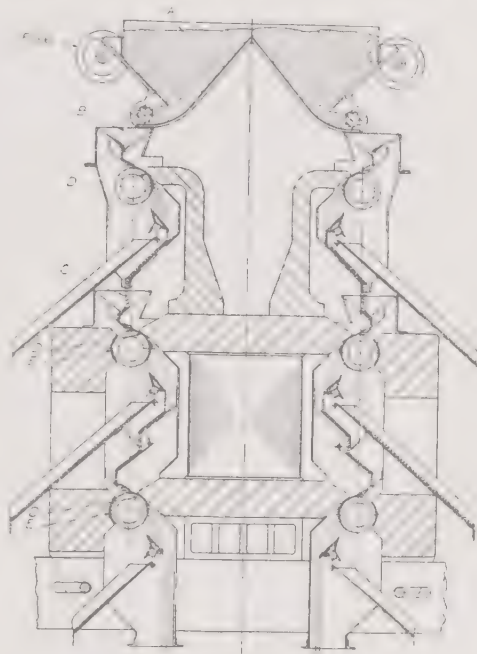
Dust Collectors. The gases from a blast furnace carry with them particles in the form of dust; the greater part of this dust may be recovered by passing the gases through a dust collector, such as shown in Figure 244. The dust collector provides a space wider than the flue, in which therefore the velocity of the gases is reduced, and their carrying capacity correspondingly lessened, so that the dust deposits. Provision is made to feed the dusty gases along the walls on which the dust may deposit, and to draw

⁴ The shelf drier may be used at atmospheric pressure, and it may be circular and provided with rotating arms; for several shelves, the material may be moved from one shelf to another with central, then circumferential discharge; compare Chapter 4 under anhydrous sulfate of soda.

ing clean gas from the center, as far from the deposited or falling dust as possible. The dust collects in the cone and may be drawn out at intervals. The dust collector has no moving parts. There are several designs. The principle is the same for all.

The **Cottrell Precipitator**. There are dusts, however, too fine to settle in the dust collector; furthermore, many gases carry fumes, finely divided solids, or metallic particles just condensing from the vapor state, which the dust box will retain. Until some 20 years ago, there were no practical means to collect the particles in such fumes, but this may now be done by means of the Cottrell electrical precipitator. The gases are passed up a pipe in which a copper (or lead-covered copper) wire is suspended; a high-

FIGURE 244.—Electromagnetic twin separator, type KT, with twin hoppers, twin feedrolls, and three high intensity induction rolls to each side. (Courtesy Stearns Magnetic Manufacturing Company, Milwaukee, Wisconsin.)



direct current passes from the wire to the surrounding tube or pipe; gases of solids present in the gas are electrified by the silent discharge from the central wire, and are then attracted by the pipe, which has the opposite polarity. The gas issues from the top of the pipe free from dust. The same principle is the same. The solids deposited on the walls of the pipe are caused to drop off into the box beneath by rapping. Not only pipes, but rectangular spaces are suitable, with several central wires. A sketch of a single pipe used in preliminary testing is given in Figure 243. The voltage is used as high as possible, without causing a spark to pass; a distance of 4 inches, such as that in an 8-inch pipe with central wire, 5,000 volts may be used; for larger pipes, 100,000 volts; higher voltages than the latter are not the practice. High voltages for direct currents are produced in a round-about way; an alternating current is stepped up by an oil transformer (2 coils laid in oil), and mechanically rectified by means of a rotating cross driven by a synchronous motor. There is taken

off the rectifying device an intermittent unidirectional, high-potential current, suitable for the precipitating pipe.

For treating large volumes of gases, enough pipes of the standard 15-ft. length must be used to lower the velocity of the gas sufficiently to clean it; this velocity differs with the content of suspended solids or mist; an average would be 4 feet per second. A treater may consist of 60 or 100 pipes, which receive the dirty gas below, and deliver to a central flue the cleaned gas at the top; if one treater is not sufficient, a second one, or a third is installed. For very large volumes, rectangular passages are better suited.

The electrical cleaning of fumes, fogs, and smokes, as it might also be called, has been applied to smelter gases, to sulfuric acid mists, to roasting furnaces, cement furnaces, and other cases. Undesirable gases such as sulfur dioxide are not retained by the treater; but cleaned of solids, the discharge is invisible, and causes less difficulty. In many cases, the material recovered has been salable and has paid for the installation; in other cases, the removal of a nuisance has prevented a shutdown by court order. The quantity of current used is not very great; for 250,000 cubic feet of gas per minute at 100° to 200° C., the power consumption was 120 kilowatts.⁵

The Magnetic Pulley. The magnetic pulley (Dings⁶) is a device widely used to separate admixed old iron from non-magnetic materials, such as crushed bones, slaughter-house refuse, glass, and many others. The pulley is placed at the turn of a conveyor belt; the bones drop off at the turn, but the iron is carried a short distance along the under side of the belt,

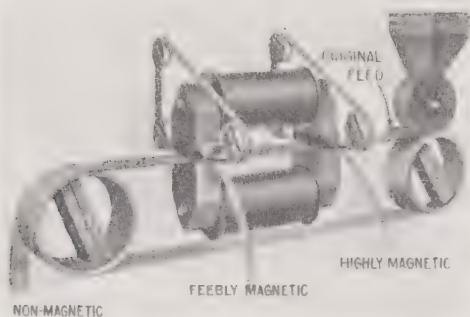


FIGURE 245.—The working principle of the Rowand-Wetherill cross belt separator. The magnetizable matter jumps up to the upper traveling belt, which carries it out of the field and drops it into a separate bin. (Courtesy Dings Magnetic Separator Company, Milwaukee.)

a point just outside the magnetic field; there they drop off in a separate container. The pulley contains coil windings and iron; the coils are supplied with direct current through contact rings protected from dust and brushes (hollow shaft). The pulley is generally a driving pulley.

Magnetic separations of solids is performed by other devices, such as the Rowand-Wetherill cross belt separator, which in turn is being displaced by the high intensity induction rolls type machine, as for example the Stearns Type K separator, the Exolon, the Dings. The induction rolls type machines have greater capacity.

Mixers. A solid may be kept suspended in a liquid by means of rotating arms. In order to mix thick liquids, such as greases, the mixing arms

⁵ "Problems in smoke, fume, and dust abatement," F. G. Cottrell, pp. 653-685, in the *Scientific Report* for 1913, with 37 illustrations and photographs. The power consumption here is taken from p. 678.

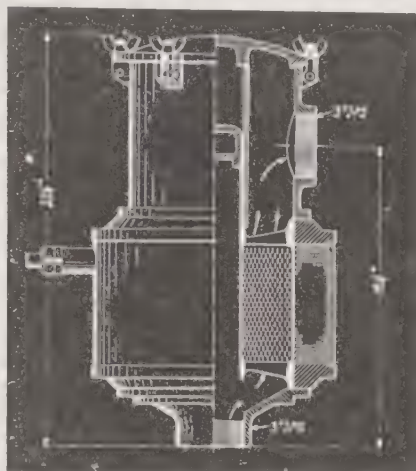
⁶ The Dings Magnetic Separator Co., Milwaukee, Wis. Similar equipment is made by the Stearns Magnetic Manufacturing Co., Milwaukee, Wis.

made to rotate in opposite directions; in general, the vessel used is heated, so that heating may be furnished. It is essential to thorough and mixing, as well as to rapid heating, that the walls be scraped. (See 246.)

The Slurry Thickener. A slurry may be thickened by settling it, run-off part of the water, and running off to the next operation a slurry in solids than the original one. The Dorr thickener is a settler with means for the continuous discharge of the thickened slurry, overflow of the water or thinner slurry, and constant feed of the original slurry. It consists of a tank with a bottom sloping toward the center, and 4 arms with scrapers, rotating slowly so as to drive the thick mud to a discharge pipe;

FIGURE 246.—An electro-magnetic separator for liquid; a partial cross sectional sketch of a Ferro Filter for liquids, of the pipe line type. As shown, the liquid travels upward through the screens which are magnetized by the coil surrounding them.

(Bulletin 15, S. G. Frantz Company, Inc., 161 Grand Street, N.Y.)



in slurry overflows from a point near the side wall and near the top, the original slurry enters at the center of the top layer. The Denver, Lange, and other thickeners are made in a number of designs, and with several working shelves if desired.

The Graver Continuous Clarifier is especially adapted to sugar juices and similar liquids. It has generally 5 shelves or compartments, and slow-moving arms with plows. The muddy liquor enters down the center; the liquor flows out at the upper part of each tray, at the circumference, and the thickened sludge flows down also at the circumference, but in a separate channel from the base of each shelf. There are numerous additional specialized settlers and thickeners on the market, each with its special

The Dorr classifier will be found described in Chapter 49, under copper, and will serve as type for classifiers in general.

The Flaker, or the Chip Machine. The production of chemicals in chip rather than in lump form has been possible by the employment of the chip machine. It consists of a hollow drum, cooled with water (or brine), in which a fused salt is distributed evenly by a small trough at the top and a larger dipping trough at the bottom; the drum turns at a slow rate,

slow enough for the salt to congeal, and the thin solid layer formed scraped off by a stout knife running the length of the drum; as the layer falls to the movable bin below, it is broken into smaller pieces, easily sliced into drums, easily dissolved by the consumer, readily weighed out to given weight, and more uniform in quality. The cylinder may rotate smoothly, turned by a gear wheel, or it may move by jerks, by means of a ratchet. The thickness of the chips or flakes is controlled by the rate

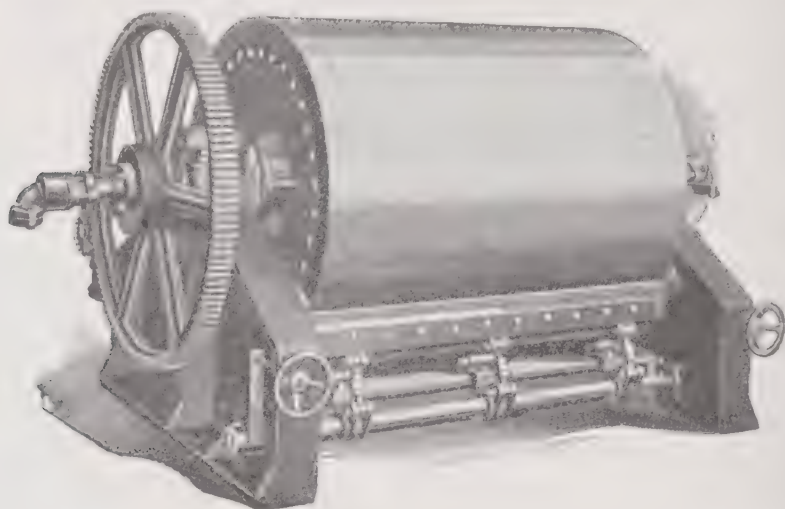


FIGURE 247.—A flaker, or chip machine. (Courtesy Buffalo Foundry & Machine Co., Buffalo, N. Y.)

feed. Occasionally one difficulty is that the layer sticks to the roll so well that the knife does not peel it off readily; there are various remedies, of which one is to place some paraffin in the lower trough. A lower temperature within the drum may also prevent sticking.

OTHER PATENTS

U. S. Patent 2,040,431, fractionating apparatus, with 2 figures; 1,889,349, a magnetic separator especially adapted for use in connection with coal crushers; 1,885,717, magnetic separator especially adapted for separating gold and other magnetic material from sand, etc.; 1,836,252, a magnetic separator; 1,857,884, precipitator, whereby solid or other material, the solubility of which vary with temperature, is precipitated by changing the temperature by means of heat transfer; 1,884,726, an evaporator comprising an upright dome especially adapted for evaporating milk (Kerner); 1,885,444, apparatus for continuous evaporating or distillation employing a vacuum and of short heating period; 1,907,197, continuously precipitating dust collector; 1,821,842, dust collector for collecting the dust from grinding, sanding and polishing machinery by passing through a chamber containing baffle plates; 1,844,591, dust collector for cement mills; 1,906,534, crystallizing apparatus consisting of a high vertical shell agitator within the shell and a means of removing the crystal from the bottom of the shell; 1,860,741, a crystallizer in which a supersaturated liquid is passed through a suspension of crystals of substance to be precipitated; 1,810,217, a continuous crystallizer using a helical ribbon conveyor to prevent adherence of crystals to the surface as well as carry the crystal and liquor through the crystallizer; 1,884,727, a drier in which material to be dried is deposited in a thin film on the periphery of an internally heated drum and then scraped off the drum (Kerner); 1,867,465, a separator and means for extracting grit and dust from air; 1,882,405, a rotating drum especially suitable for drying silica.

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Frequently the success of a new process depends not upon the correctness of the chemical calculations, but on the proper choice of the mechanical device which automatically brings the raw materials to the reaction chamber, or on the device which, again automatically, takes the product away; for an industrial operation must be profitable or it cannot live. It will be apparent that the importance of an acquaintance with the ordinary mechanical devices which an industrial chemist needs cannot be overestimated.

Chapter 44

Appliances Used by the Chemical Engineer IV. Crushers, Disintegrators, Pulverizers

The handling of liquids and gases is a comparatively simple matter; applying pressure at one part brings a quick response from every other; they are of uniform texture; where one part will pass, all the others will. Not so with solids; pressure at one end of a long pipe filled with a solid of assorted sizes would only jam it fast, except for an impalpable powder. Solids must be carried all the way from one spot to another in a wheelbarrow, or in a succession of little barrows or buckets which deliver their load and return to the starting point for another. By making the chain carrying them an endless one and running it over two sprocket wheels, upward and with the load, on one side, and down, empty, on the other, we achieve the automatic elevation of a solid in its simplest form, that of the *bucket elevator*.



FIGURE 248.—The bucket elevator. *F*, feed; *D*, discharge.

vator; traveling vertically, it lifts coarse solids to an elevated delivery point. The chain and buckets are enclosed in a steel housing which prevents loss and dust nuisance; the housing has a feed hopper at the bottom, also called the boot; the buckets pass through the solid; a delivery spout is also part of the housing, at the top. The operation is indicated further in Figure 248. The chain is usually belt-driven; the driving pulley is part of the upper sprocket shaft; the lower sprocket is merely an idler. The buckets are of various sizes, rarely over 4 inches by 8 inches; the travel is slow, about one foot a second, and the capacity rather small.

When a large capacity is needed, an elevator on which heavy barrows may be loaded is used, or a skip hoist.

In the form most commonly used in chemical operations, the buckets in the bucket elevator are at some distance from each other; there are also those bucket elevators in which the buckets shoulder each other, and cover the chain completely. The other extreme is a form which has only two buckets, of large size, which are so disposed that one descends as the other ascends; both reach the end of their respective trips simultaneously; this type is called the *skip hoist*. It does not include an endless chain; the bucket is really a small car traveling on inclined rails, which is pulled up the incline by a drum-wound cable. The skip hoist has no casing. It is used, for instance, for lifting ore, coke, and limestone to the top of an iron blast furnace.

The Conveyor. In order to move solids from one point to another on the same level, conveyors are used; among the various types may be mentioned the belt conveyor, made of leather or reinforced rubber; the screw conveyor, usually of metal, and the pneumatic conveyor.

The belt conveyor is well adapted to long trips, that is, 100 feet or more¹; if the material must travel along one level, then up an incline to an elevated level, and still another distance along the upper level, a belt conveyor in a single piece will give the required service.

The belt conveyor is pulley-driven, and rests on small rollers or idlers; on the up-travel the loaded belt passes over auxiliary idlers placed under the two edges slant-wise so that the edges are turned up slightly; the solids cannot roll off. The speed is not high, perhaps one foot in two seconds, but the capacity may be made high by using a wide belt.

By causing one belt to dump its load on a second one traveling at right angles to it, the material carried is made to turn a corner.

For moving solids along the level, screw conveyors are used, if the distance is short. They consist essentially of a wide sheet-metal screw fitted in a gutter with rounded bottom; the screw shaft is driven by a pulley; as it turns it pushes the solids along the gutter, until they reach an opening which delivers them to a bin, for instance. Vertical screw conveyors are also in general use for special services. Two remarkable conveyors are the Redler "en masse" conveyor, and the Johns split rubber tube conveyor.

A pneumatic conveyor is used for elevating solids, for example for conveying loose soda ash from a box car to a steel storage tank placed on the roof to permit feeding to various dissolvers by gravity. The installation comprises a suction pump protected by a dust collector, an air-tight steel pipe, and the suction line, partly steel, and partly of rubber, ending in a receiver which is introduced in the car. The fine powder mixed with air travels up the pipe until it reaches the bin when it drops, because the velocity of the air drawn in is reduced. The air travels further to the dust collector, then to the pump.

The Fuller-Kinyon pump, mentioned elsewhere, is a pneumatic conveyor.

Poidometer. The poidometer is a device for the continuous weighing of a loaded moving belt, with regulation of the load. The device is placed

¹ A belt conveyor four miles long is described in *Chem. Met. Eng.*, 32, 159 (1925).

at the base of a bin, with a small hopper of its own. The belt rests on a pulley which actuates a beam with weights. The beam in turn actuates the gate from the hopper; if too much material is fed, the pulley is depressed, the beam rises, and the gate drops. The graduation on the scale is in pounds.

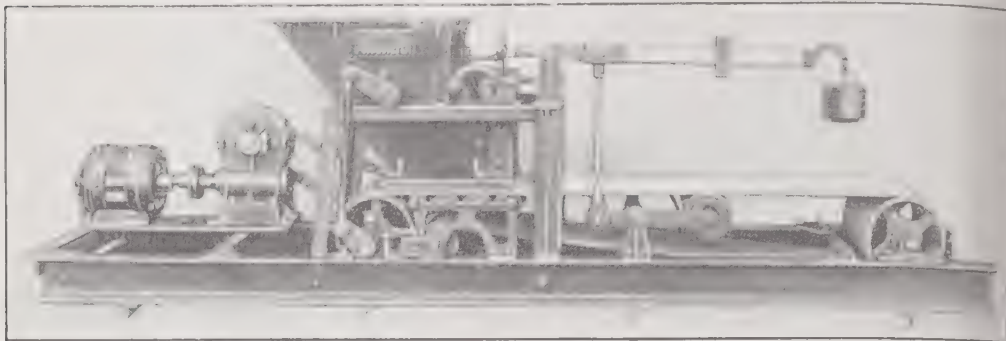


FIGURE 249.—The essential parts of a poidometer. (Courtesy of Schaffer Poidometer Co., Pittsburgh, Pa.)

per running foot of belt; a separate device records the running feet of belt, so that total poundage is automatically recorded, and with proper setting, assured. The accuracy is within 1 per cent. The capacity varies with the size of the poidometer and with the bulk weight of the material; it may be 1 pound per minute or 10,000 pounds per minute.

CRUSHING, DISINTEGRATING, AND PULVERIZING

A distinction is made between crushing, disintegrating, and pulverizing; the lines cannot be drawn with accuracy, for usage differs; for the sake of clearness the distinction will be assumed to be definite. In general terms, crushing means the reduction of large pieces, such as a man can just carry, to egg and nut sizes; the reduction of egg and nut sizes to a coarse powder is termed disintegrating, also grinding; finally, the reduction of the coarse powder to a powder so fine that the separate granules cannot be felt between the fingers is termed pulverizing; these latter fine powders are aptly termed impalpable.

The sizes resulting from these operations are never uniform; a mixture of sizes is obtained which must be graded by sieving or screening; the definition of sizes is then made in terms of the percentage which will pass through a given screen, the remainder being termed "on the screen." Sieves and screens are described by the number of holes or meshes to the lineal inch, if small, or by the dimension of the hole in inches if large; the holes are regular, either circular or square, hence giving the number to the lineal inch defines them. The circular holes are made by punching a steel plate; the square holes are made by weaving iron or other wire, and are called meshes.

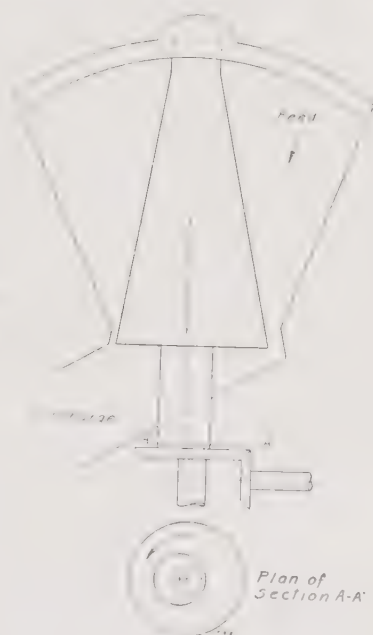
The distinction above may then be repeated in terms of meshes. Large lumps are "crushed" to pass through a three-inch mesh; "disintegrating" means reducing the size so that 90 per cent, or so, will pass a ten-mesh screen, that is, through a screen having ten meshes to the inch; "pulver-

"g" means reducing so that 90 per cent, or so, will pass a 100-mesh screen better, that is, will pass through a screen having 100 meshes or more to an inch.

Crushing is done in gyratory crushers, jaw crushers, and rolls; disintegrating is done in pot crushers, rotary-hammer mills, squirrel-cage disintegrators, and stamp mills; pulverizing is done in bulrstone mills, suction mills, ring-roll mills, pebble mills, and edge runners. There are many other special devices in addition to the ones listed which are used for reducing the size of a solid. Modifications of those given fit them for two classes, in general the devices are listed as they would come to the mind of a man when the three classes of service are mentioned.

The Gyratory Crusher. The gyratory crusher is a pot crusher in which the gyrating element is set slightly eccentric to the pot in which it works. Figure 250 indicates its construction. The rock slides down in the wide opening made at the half-turn when the space is widened; at the next half-turn the space is too narrow to accommodate the piece and it is crushed. The gyrating element is smooth, or grooved. In size the gyratories are built with gyrating elements from 3 inches in diameter to 72 inches; the large ones are the best known. The crusher with the 72-inch crushing head

FIGURE 250.—The gyratory crusher, a pot crusher with the gyrating element set eccentric to the pot.



5 feet over all, makes 175 r.p.m., and requires 300 to 500 horsepower. It is usually belt-driven; when an unbreakable object finds its way into the crusher accidentally, the belt slips and no damage is done to the gears. The various sizes are well adapted to reduce the large lumps brought from a mine or from the quarry, such as gypsum and cement rock, to egg size.

The Jaw Crusher. The jaw crusher has a back-and-forth motion; here the lump slides down as the space widens and at the next forward

stroke is crushed to smaller sizes. It is a powerful crusher; its crushing plates vary in size from 2 by 6 inches to 12 by 26 inches and over. It is most commonly used in medium sizes. To prevent injury when an unbreakable object finds its way between the jaws, a weak point is provided by connecting the moving jaw to the driving shoulder by a slender rod



FIGURE 251.—The jaw crusher.

which breaks, and which is quickly replaced after the foreign object has been removed. The translation of rotary motion to the back-and-forth motion is by means of an oval, mounted on the pulley shaft, as indicated in Figure 251.

The crusher with plates 12 by 26 inches makes 140 complete strokes, that is, back-and-forward trips, per minute; it requires 25 horsepower; crushing to pass $1\frac{1}{2}$ -inch mesh its capacity is 12 to 15 tons per hour, half a carload; crushing to pass 2-inch mesh, 20 to 30 tons per hour. The greater capacity of the coarser size is due to the wider spacing between the jaws, which permits more material to pass through.

The Rolls. Rolls are used in many sizes, usually double, the rolls rotating toward each other; their surfaces are corrugated or spiked. (Fig. 252). They are well adapted to materials which crush easily, such as coal,

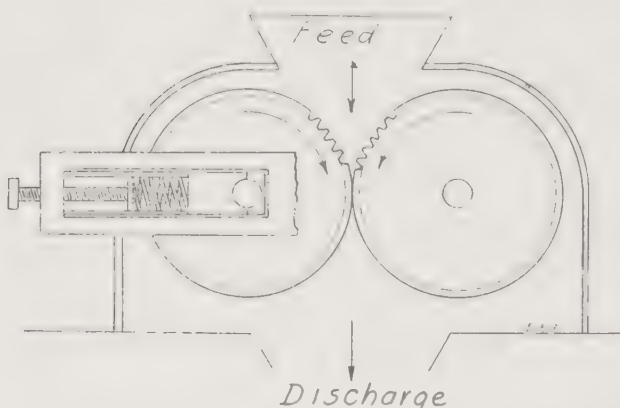


FIGURE 252.—Crushing rolls.

bones, or coke. Provision against destruction is made by mounting one of the two rolls in journal boxes which can be forced back against stiff springs in case an unbreakable object is introduced; through the temporarily widened space, it drops through, and the normal spacing is made again. Perhaps it should be added that the shafts of the rolls are horizontal, the material is fed in from above, and passes through by gravity. The operation

will be clear from the drawing. Instead of two rolls, a single roll working against a fixed plate may be used. The capacity of a roll crusher is high.

Rotary Hammer Mills. A comparatively new type of disintegrator is the rotary hammer mill, of which there are many variations. The mill shown in Figure 253 is the Jeffrey; it is one of the three best-known types, the other two are the Williams and the Gardner.

The hammers are steel bars free to pivot on a pin inserted in a central integral with the horizontal shaft. As the disk rotates, the hammer is whipped with great force against the incoming lumps; these are caught between the stationary breakers plate, of manganese steel, and the whirl-hammers. The solid is reduced to small sizes which pass down through a semi-circular screen forming the lower part of the casing. The speed of the shaft is high, between 600 and 2500 r.p.m., so that to describe them as cyclonic is rather apt. A long list of materials may be treated in these mills, including asphalt, nitre cake, gypsum, lime, bone for casing, and steel, cottonseed press cake, cinders, clay, and clam shells.

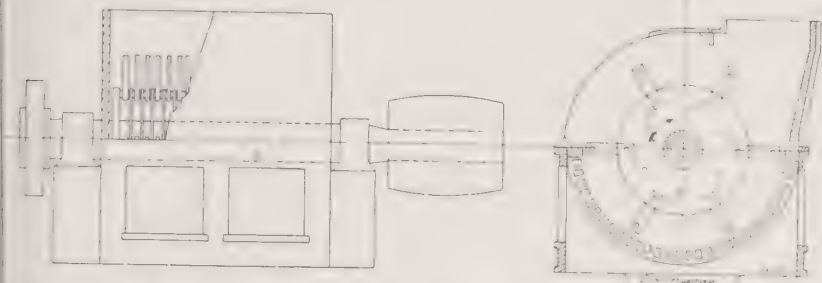


FIGURE 253. The Jeffrey crusher, illustrating the rotary hammer mill type of disintegrating device.

No provision is necessary against unbreakable objects of small size; the hammers can bend back and pass over them; the decreased discharge will indicate that there is an obstruction.

The hammers wear fast; in order to get as much use out of them as possible several holes are provided in the disk, so that they may be moved toward the edge as they become shorter; at the stage shown in the figure, they are quite short, and have been moved twice.

The shape of the hammer varies with the use intended; it may be a straight bar, a twisted one, blunt or sharp; it may be a yoke instead of a bar of manganese steel, free to pivot like the plain bar.

The *pot crusher* is one of the older types of disintegrating device. Its section is the same as that of the gyratory except that its rotating disk is centered.

In the *squirrel-cage disintegrator*, two circular cages of steel bars are mounted on steel rims, concentric, rotate in opposite directions. The material to be disintegrated is fed in the center, and must pass between the two cages. The squirrel-cage disintegrator is used to prepare coarse

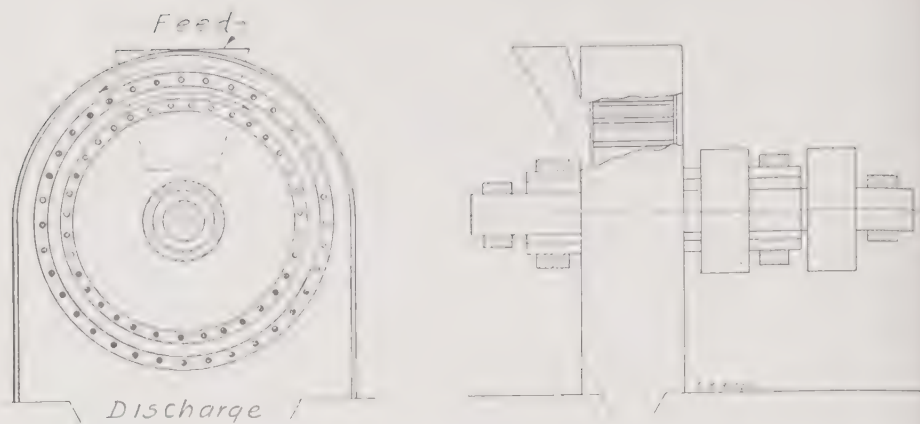


FIGURE 254.—The squirrel-cage disintegrator.

powders, for instance, ground nitre cake sold in cans for household use; the powder must not be too fine, and no uniformity of size is sought.

The *buhrstone mill* is one of the oldest pulverizing devices. Formerly it was used by the millers for preparing flour; in the large mills of the Middle West it has been displaced by special corrugated rolls which tend to elongate the wheat kernel rather than pulverize it. In the chemical industries it is rarely used.

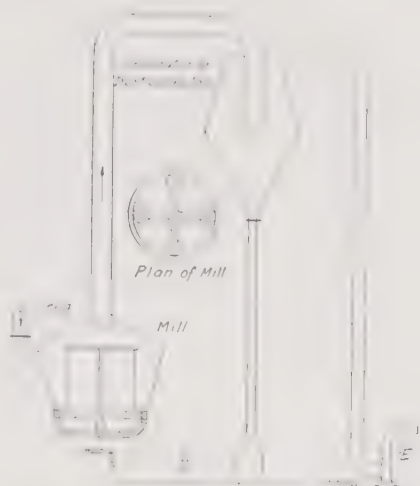
The Suction Mill. In the suction mill, the material is ground between rotating horizontal wheels of small diameter, thrown by centrifugal force against the inner face of a larger, stationary ring; the material must be so fine that a current of air drawn through the mill can sweep it along as a fine dust; until that fineness is reached, the material remains subjected to the action of the mill proper.



FIGURE 255.—The buhrstone mill.

The best-known mill of this type is the Raymond. It consists of the mill proper, a dust collector, and an exhaustor. In the mill four small wheels are suspended from the arms of the vertical shaft in such a way that they are swinging freely; the centrifugal force presses them against the grinding ring, as shown in Figure 256; here the grinding, or better, pulverizing, takes place. The speed of the shaft (vertical) is about 100 rpm. Air is drawn in through the feed box or through the floor of the mill; the fine powder, really dust, is carried up the pipe into the dust collector separator; here the dust is deposited, and the air, now free from solids, passes to the exhaustor. It is rare that the discharge from the exhaustor

FIGURE 256.—The Raymond mill, illustrating the suction type of pulverizers. *E*, exhaustor.



the dust, and that is one reason why this air is frequently led back to the mill again, entering below the stationary ring.

The Pebble Mill. The pebble mill in its simplest form consists of a plain jar containing a few pebbles; by placing it on the arm of a wheel it may be swung in a circle. As the pebbles glide, the pulverizing process takes place.

The industrial mill is closely modeled after the simple mill above; a container, which may be tulip-shaped, replaces the porcelain jar; it contains three or four iron balls for a container 24 inches in diameter. The material passes through the long axis of the tulip, and is inclined at an angle of 30°.

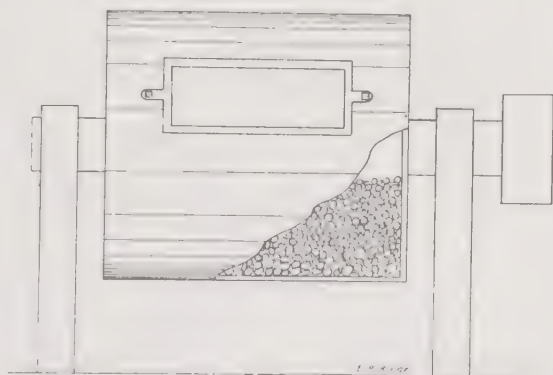


FIGURE 257.—A pebble mill for intermittent operation.

The best-known pebble mill in the chemical industries has water-worn pebbles about $2\frac{1}{2}$ inches in diameter, as nearly spherical as possible; they occupy one-third the space in a hard steel cylindrical container 4 feet long, 4 feet in diameter or larger; revolving on its horizontal axis (see Fig. 257).

When a batch of material is placed in the mill, the cover clamped down and the mill revolved at a speed of 60 r.p.m. After a period, the mill is stopped;

the cover is replaced by a grid which permits the powder to pass, but retain the pebbles; the mill is revolved again and gradually discharged into the hopper beneath.

This periodic operation may be changed into a continuous one by feeding and discharging through the trunnions; such a mill is the Marcy.

The Hardinge continuous pebble mill is pear-shaped, with the long axis horizontal; the feed (and discharge) is through the trunnions. It revolves at rather higher speed than the cylindrical mill, and has several sizes of pebbles which "classify" themselves; this mill is used for example for pulverizing Florida phosphate rock after a preliminary treatment in a disintegrator.

A tube mill is a cylindrical pebble mill whose length is several times its diameter.

The Edge Runner. The edge runner is one of the older devices, still much used, but less than formerly. Its function is partly that of a pulverizer, partly of a disintegrator. It consists of two circular stones about three feet in diameter, and eight inches wide, running on the eight-inch face. (See Fig. 258.) They are carried on the two horizontal arms of a

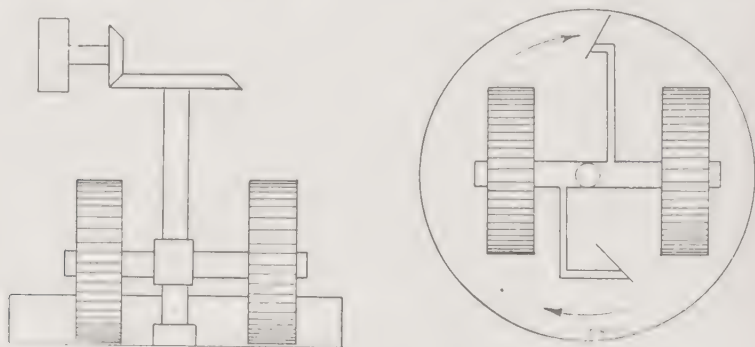


FIGURE 258.—The edge runner.

vertical shaft, and are placed on opposite sides. As the shaft rotates, the stones are pulled around, and as the line of travel constantly leaves the vertical plane of the stones, there is a side-wise drag which grinds, in addition to the crushing due to the mere weight of the stones. The material lies in a shallow pan; the operation is either batch operation, that is intermittent, or continuous, by means of slight alterations. Small plates sweep the material into the path of the stones.

Instead of rotating the stones in the stationary pan, the stones may be left stationary, and the pan rotated; also, corrugated steel cylinders of similar proportions may be substituted.

CHOICE OF APPLIANCE AND SEQUENCE OF OPERATIONS

Crushing operations frequently involve two or more devices; for instance in a coke plant, the coal passes crushing rolls first, and the product is sent to a Gardner crusher, of the rotary hammer-mill type, which reduces the egg size to a coarse powder; this is then loaded into retorts. In a gypsum plant, the rock from the mine passes through the gyratory, then the Jeffrey

finally the Raymond mill; by these three steps, lumps of rock are reduced to an impalpable powder. Sometimes a single device is sufficient, for instance when sodium sulfide melt is made into cakes about three feet square and six inches thick, such a cake may be broken in several pieces with a sledge hammer, and the pieces fed to a jaw crusher set for rather fine crushing; the product is fine enough for leaching tanks.

The choice of the crushing, disintegrating, or pulverizing device depends largely upon the desired fineness, but other factors must be considered. One is the toughness or brittleness of the material; another is whether very fine products are desired, or the greatest possible amount, with few coarser sizes. From any device, a single size is not obtained, but an assortment;

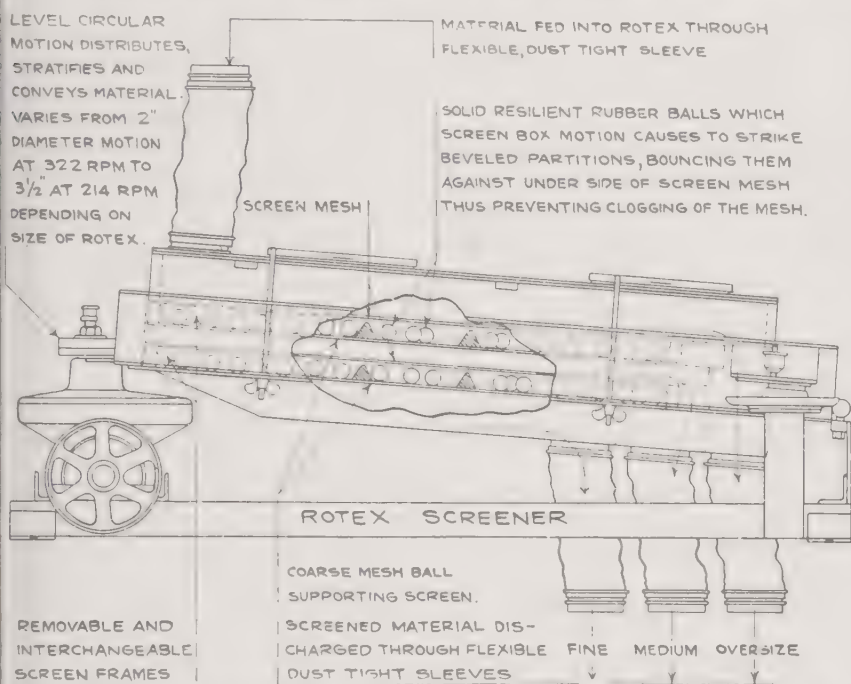


FIGURE 259.—Flat screen with rapid rotary jerky motion, and with tapping.
(Courtesy Orville Simpson Co., Cincinnati, O.)

tain one size, screens are used; the total product of the crusher is run through the screen; that which passes through proceeds to the next operation; that which remains on the screen, the tailings, returns to the crusher.

Screens. For small operations, a hand screen is used; it may be made by attaching a wire netting to a four-sided wooden frame. Placing the material on the screen and moving the whole mass back and forth, a part of the solid will pass through and a part will remain on the screen, if properly chosen. In screening operations of the automatic type, some motion is required. Otherwise the mass lies on the screen and clogs it. Some automatic screens give this motion by revolving and so moving the solids; others are fixed, stationary, but receive rapid blows which constantly dislodge the material, causing the tailings to roll down the incline. The Moto-Vibro

screens of the Sturtevant Mill Company are of this type. Usually the sizes are sorted by means of two screens, the coarser screen being placed over the finer one. The fines pass both screens; the middlings pass the upper but not the second; they run to the low point where a chute or a screw conveyor transfers them to the next device; the tailings cannot pass either screen and are returned by means of a chute and a bucket elevator to the disintegrator.

The mechanically developed vibration may be a "positive circle throw" motion, or a reciprocating motion. A number of screens are electrically vibrated. For the fine sizes, the grading may be done by *air separator* which sort by the floating quality of the particles; example, the Sturtevant Air Separator. The air separator is valuable especially in close circuit grinding in which the suitable fines are collected and the tailings returned to the mill.

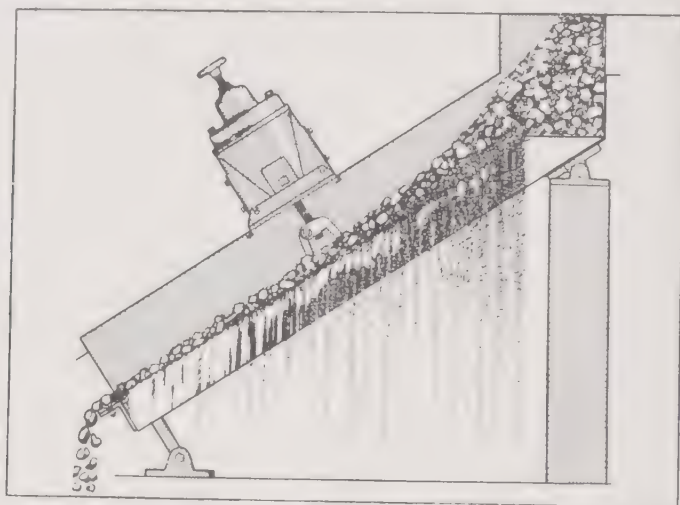


FIGURE 260.—Cross-sectional drawing of a one-deck electrically vibrated screen, the Hummer, showing the principle of operation. The stratification of the materials causes the fines to hug close to the screen, while the coarse particles travel on top. (Courtesy The W. S. Tyler Company, Cleveland, Ohio.)

In the Blutergess high speed turbine sifter, a still different principle is applied. There is no shaking, no vibrating, no suction. The material is thrown by a central turbine against the cloth. The motor is $1\frac{1}{2}$ h.p.; the surface of the stationary screen is $6\frac{2}{3}$ sq. feet; yet the capacity is high. With a speed of 740 r.p.m., and a 110-mesh screen, 550 pounds of precipitated sulfur are screened per hour. With 1400 r.p.m., and a 60-mesh screen, 2000 pounds of aluminum stearate are delivered through the screen per hour.

The *rotary screen* may be cylindrical, of the same diameter throughout when it is usually given a slight incline toward the discharge end. It is mounted by slender arms to a central shaft, which is rotated slowly. The material is fed to the inside of the screen; as the screen rotates, the solid travels further and slightly down; the fines pass through the meshes. If the screen has two sizes, the smaller mesh is first; using hypo crystals

* About 60 r.p.m. for a screen 36 inches in diameter and 140 inches long.

example, the fine powder would pass through first, the pea size and lumps would roll on. At the second size mesh, the pea would drop off and would collect in barrels, free from either fines or lumps. The fines pass all the way through the cylinder, and drop off at the lower end. Instead of being cylindrical, the screen may be wider at one end than the other; the material enters at the narrow end, and as the screens revolve around its horizontal shaft, it moves downward toward the wide end where the tailings are discharged. Such screens are used for heavy materials such as gypsum rock or pyrite.

OTHER PATENTS

U. S. Patent 1,859,499, rotary drum ball mill in which pulverized material is removed by a current of air or fluid; 1,879,479, ball mill for carrying out reactions in the presence of sulfur fusions; and 1,862,557, same; 1,840,380, pulverizer of the rotary beater type; 1,862,889, a rotary crusher with screening grid; 1,888,636, cylindrical screening concentrating apparatus having rotary motion; 1,882,908, inclined vibrating screen; 1,879,499, horizontal rotary screen or trommel; 1,798,433, rock crusher having an eccentric operating mechanism, and a shaker screen having its receiving end mounted eccentric of the crusher; 1,884,316, crusher of the rotary type applicable to various constructions; 1,874,830, jaw crusher consisting of a movable and a fixed jaw; 1,872,233, hammer mill crusher; 1,847,859, a double roll crusher; 1,871,727, apparatus for disintegrating particles suspended in a liquid; 1,764,138, hammer mill having a series of hammers which crush the material as it moves along on a belt (not having cage bars); 1,762,727, grain disintegrating mill consisting of one movable and one fixed attrition plate.

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 "Crushing and grinding," W. F. Carey, *Trans. Inst. Chem. Eng. (London)*, 12, 179 (1934).
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 "Crushing in the process industries," Albert E. Reed, *Ind. Eng. Chem.*, 30, 1369 (1938).
 "Electrostatic separations of solids," Foster Fraas and Oliver C. Ralston, *Ind. Eng. Chem.*, 32, 600 (1940).
 "A review of certain unit processes in the reduction of materials," J. C. Farrant, *Institution Chem. Eng. (London)*, 18, 56-75 (1940), with an appendix on "The theory of screening," by R. F. Davis, p. 76.

Among the many tasks which devolve upon the chemical engineer is that of finding vessels in which the reactions of commercial importance may be run. The requirement is never that the vessel should last for many years but merely long enough so that its cost may be absorbed by the process; it follows that a cheaper vessel may be replaced more often than a dear one, and that a valuable product will permit a more expensive reaction vessel than a product selling for a low price. A second consideration is that the time lost for replacement must be as short as possible, for while the plant is idle it earns nothing.

Chapter 45

Materials of Construction Used by the Chemical Engineer

The materials used by the chemical engineer are very numerous; of first importance are steel, cast iron, wood, stone slabs, bricks of various kinds, lead, copper, and stoneware. These materials serve for the construction of reaction vessels, absorbing and collecting vessels. The subject of bricks is inseparably connected with the cement in which they are laid; the cement must resist the attack of the reaction mass as well or nearly as well as the bricks themselves. Of secondary importance in point of tonnage are the special alloys such as Duriron, Monel metal, bronze, quartz, glass-lined cast-iron vessels, and others. A third class of substances is the filling materials in towers for the absorption of gases in water, or for the drying of gases by means of sulfuric acid for example. A fourth class might be that of the catalysts, such as platinum and iron. A fifth class is the adsorbents such as charcoal in the Burrell process for the removal of gasoline from natural gas. All these classes are used by the chemical engineer; the divisions are for the sake of clarity chiefly. But besides making the materials it must be shipped, and suitable containers are essential for the full development of a manufacture; glass, lead, steel, wood, absorption of diatomaceous earth, even wax, are concerned in the development of shipping containers.

Unlined steel is used wherever possible; storage tanks of considerable size are built of mild steel sheets, riveted or welded; the sheets with proper curvature and with the rivet holes punched, are shipped by rail and assembled on the spot, so that there is no limiting size in transportation which interferes. With cast iron, it is different; unless the piece is made in sections, bolted together on the job, its size is limited by the size of the railway cars. Unlined steel is used for the storage of oils, ammoniacal liquors, alcohol, concentrated sulfuric acid, mixed acid, and oleums, besides countless other liquids; it is the reaction vessel for the recovery of ammonia from the ammonium chloride liquors in the Solvay soda process, for the distillation of industrial alcohol and methanol, for the soda wood-pulp digester, and many others. Cast iron is used for caustic¹ pots, for the final cooling

¹References to other chapters would be so numerous in the discussion of materials used by the chemical engineer that they will not be given; the reader will please consult the list of chapters at the front, or the index.

ration to the anhydrous condition over the free flame; for nitric acid tests, and Mannheim furnaces for hydrochloric acid; for the nitration and sulfonation of benzene and other organic substances; and for many other reactions. Cast iron is not as strong as steel, which is one reason why it is generally greater in wall thickness. It has, however, this great advantage, that it can be cast to any curved shape desired, and may have internal weirs, and partitions. If the casting is to be water-cooled, internal passages may readily be arranged to permit the necessary circulation.

Castings are comparatively cheap.

Castings (Iron). In a foundry, pig iron is the main raw material; it is of a specific quality, and a certain definite proportion of steel scrap is added which among other things lowers the carbon somewhat. The pig iron with added steel is melted in a cupola, essentially a small blast furnace with an hourly capacity of 10 to 15 tons. The fuel is coke, and a small amount of flux (limestone) is provided, whose function it is to form a slag with the ash from the coke and any sand adhering to the pigs. The iron passes through the cupola practically unchanged in composition; the carbon, combined and free, remains the same; the silicon decreases somewhat, the sulfur increases slightly. The loss in iron is 5 per cent, chiefly in the form of iron oxides mixed with the slag.

The melted iron is drawn into ladles carried by overhead cranes (electric), and poured into the prepared form. Small castings are made in "flasks," two-piece boxes filled with sand in which the impress of the design is made. If in one part, half in the second part; the inner part of the casting which is to be hollow, is represented by a solid shape of sand, the core; where the core is, the metal cannot flow; it can only fill the space between the flask and the core. Flask and core are made from a pattern made of wood, from accurate measurements, with enough oversize to allow for the shrinkage of cast iron on cooling, one-eighth inch per foot. The small castings are poured from a crucible on long bars carried by two men; the flask is filled from the ladle. The core is made to hold together by ramming the sand with molasses and baking till hard.

The practice in making a casting may be further illustrated by a sand casting pot, which is cast right side up, that is, with the flange on the top and the round bottom at the base. There is first constructed a core, which is made of bricks as well as sand are employed; around the core, a mold is made of sand which determines the outside surface of the casting. An extra height is provided in which the metal rises, carrying in its upper portions any slag which it may contain (the riser); this part is later cut off. The metal flows into the comparatively thin space so provided, and fills it. After some cooling, the outer wall pieces are knocked down and the pot is lifted up (annular shapes); the pot may then be lifted in turn, and then the core knocked out.²

Castings are cleaned of core sand by sand blasting or by wire brushing, and may be machined on lathes; they may be drilled and threaded. Cast-iron drillings are short, almost powdery; steel drillings are long shavings or shavings.

² Compare article in *Chem. Met. Eng.*, 20, 394 (1919), with 8 illustrations.

Steel. The steel used for storage tanks, car tanks, stills, reaction vessels, settling tanks, classifiers, evaporators, and an endless number of purposes is generally mild steel, with 0.20 to 0.30 per cent carbon. The thickness varies with the size of the vessel and the purpose. For a storage tank for alkaline liquor, 20 feet in circular diameter and 20 feet high, the sides would be three-eighths inch, the bottom perhaps one-half inch thickness. Steel tanks are riveted, single or double, and caulked by



FIGURE 261.—“Near the end of the ladle”; pouring metal for a large casting (special cast iron). (Courtesy Buffalo Foundry and Machine Company, Buffalo, N. Y.)

pneumatic chisel. The practice of welding instead of riveting is growing constantly; the weld has the advantage that it does not need caulking, and is not subject to a leaking rivet. Steel tanks exposed to the weather are painted on the outside.

Steel may be punched, as well as machined; it may be drilled and threaded; it may be bent into box-like shapes, cutting for the corners and welding the edges; two such boxes, one shallow and one deeper, are riveted together to form a jacket through which water may be circulated, the water-cooled jacket, suitable for furnace walls without any protection. Inhibitors of corrosion are briefly mentioned in Chapter 1 (see also reading references there). The suitability of steel to certain strengths of sulfuric acid will be found discussed in the same chapter.

Steel castings are poured from the bottom of a ladle; the molds may be hand-made or machine-made. Hand-made molds take longer to pre-

are and are used for larger pieces. The steel is prepared in an open-hearth furnace, most generally a basic open hearth, with capacity of 20 tons, for example; scrap steel with some pig iron makes up the charge. Additions are made in the ladle (Compare Chapter 48). A cast steel may run from 0.25 to 0.35 carbon, with specified amounts of manganese. In one plant, the molten steel is 3000° F. (1649° C.) in the furnace, 2700° F. (1482° C.) when poured. After cooling the casting is reheated, cooled to a definite temperature, and quenched in water (or oil) for a specific number of seconds. The best steel may be forged. Certain pieces are carburized.

Wood. Formerly wood was used much more than now; whenever permissible, the steel tank has taken its place. For some processes, in which dilute mineral acids are used, wood (oak) is still the best material; for example in the extraction of bones with cold dilute hydrochloric acid for gelatin and glue making. For intermediate water storage in large plants, wooden tanks are freely used. A wooden tank is made tight by swelling it with water. It will remain tight if kept filled; but if allowed to become dry, the tanks shrink, and leaks develop; in this respect the wooden tank is inferior to the steel tank. Wooden tanks lined with lead are used for storage, crystallizers, and other purposes. The present war conditions (1942) have stimulated the use of wood for many chemical purposes.

Stone Slabs. Towers for the cooling of hydrogen chloride and for its absorption in water to form hydrochloric acid may be constructed of stone slabs. Sandstones about 6 inches thick and 4 or 6 feet square are placed several days in hot tar which penetrates into the stone a short distance and renders it acid-proof; a stone 7 feet square 12 inches thick forms the shell; it is hollowed out enough to give drainage to the discharge opening at its center. The bottom stone is placed on piers, and the square tower is built up of the thinner stones, each course consisting of two 4 by 4 and two 6 by 4 stones, held together by cast-iron corner pieces and steel rods. The joint between the stones may be filled with asbestos cord, or with specially made rubber gaskets. Such towers are not used as much as formerly, but many are still in operation. Every Mannheim furnace has at least a cooling box for the gas made of tarred stones.

Bricks. The common red brick and the sand-lime brick are used for the inside and outside courses; soft or hard firebricks for the lining of fireplaces. The latter are also the more common acid-resisting bricks; they are strong, hard, and tough, and unaffected for example by the acid liquor in the sulfide pulp digester. In this digester, the bricks are laid in litharge and glycerin for cement; this mixture hardens and resists the acid liquor as well as the bricks. Until its introduction, the digesters had to be relined at frequent intervals, a costly interruption. In fireplaces, the bricks are laid in moistened fire clay, or in fire clay and silicate of soda solution. Silicate of soda is also useful, and sometimes for filling cracks between bricks in a hot furnace (with alkaline charge), sand alone; it is gradually fused by the alkali and runs into the spaces between the bricks. Portland cement with sand is used in the outside courses, unaffected by the acid charge, but may also be used in numerous cases inside the furnace. Sand and asbestos in silicate of soda is both fire-resisting, and to a con-

siderable extent acid-resisting; for nitric acid, a little linseed oil is incorporated. Some silicate of soda mixtures protected by trade names contain, besides ground asbestos and silicate of soda, some tar. "Acid-proof" cement, sold as special cement under that name, is usually ground flint, which the customer is directed to mix with silicate of soda solution. Fire clays and ground asbestos may be equally suitable.

Portland cement furnaces are usually lined with bauxite bricks, but recently unfired chemically bonded magnesia bricks have been used for this purpose. Magnesia bricks for basic Bessemers and similar processes are very resistant to slag and fused limestone. Chrome bricks are as dear as magnesia bricks (\$100 to \$200 per thousand); they are said to be neutral; slag does not cling to them.³ Somewhat cheaper alkali-resisting bricks are made from alunite.

The function of all the bricks given above is to resist heat and chemicals; a brick may be needed, however, for a totally different purpose, namely, to divide a heating chamber from a reaction chamber; in this case, it may still need to be heat-resisting, but it must also be reasonably heat-conductive. Silica bricks are such, discussed in Chapter 10, where crucibles are also discussed; it should be added that shapes, slabs or bricks made of alumina or silicon carbide are also heat-conductive, and are available though at higher cost than silica.

Lead. It may be said that it is to lead that the chemical industries owe their success; until it was employed for the reaction vessels in the manufacture of sulfuric acid, the latter product was a curiosity; it is now a commodity at 1 cent, in favorable cases 0.5 cent per pound, and even less. Lead sheets form the walls of the sulfuric acid chambers, of the Gay Lussac and Glover towers, of the storage tanks, with wooden or steel frames, for the piping of the acid, for pumps, and for the conveyance of the gases from one tower to another perhaps distant one. The lead chamber walls are supported on wooden (also steel) frames, and the sheets are burned together, that is, the edges are melted together with a hydrogen-air flame. Lead-lined steel is used for the saturation of soda ash suspension in the manufacture of anhydrous bisulfite of soda, for the pickling bath in the galvanizing plants (if sulfuric acid is the pickling acid), in ammonium sulfate saturators, and in numerous other installations. Lead sheets which have become perforated, or thin in spots, are sent to be rerolled for a nominal charge, into any thickness desired.

Lead used for chemical purposes such as those listed above is soft lead; it is not the purest lead, but contains antimony, copper, zinc, and other impurities which render it more acid-resisting. By raising the antimony content to 6 or 10 per cent, the lead is made rigid, about twice as strong as chemical lead, and remains acid-resisting. Lead-lined vessels, pipes and fittings, are also in use.

Copper. Copper is used for the redistillation of acetic acid, which does not attack it except to a slight degree; copper is used also for the steel

³ In normal times, a firebrick good for 2600° F. costs about \$47; good to 3200° F., \$85 to \$100; in both cases 4½ × 9 × 2½ inches; silica bricks, \$58 and over. All prices for 1000 bricks to the yard. Fireclay costs \$9.80 per ton (for bulk).

in crude methanol stills, and for the rectification of ethyl alcohol. Copper is the melting vessel for a number of copper alloys; the varnish is made of copper. Shelves and trays in the fractionating towers for liquid air, as well as for bubble towers in oil refining, are made of copper. Water-cooled copper coils are used in electrolytic furnaces, while water-cooled copper or copper alloy discharge pieces are suitable for fused sodium and other furnaces.

Stoneware. For acid vapors and acid liquors, stoneware furnishes absorption, and collecting vessels; it is made of selected clays, free from all coarse particles, and sintered throughout its thickness; a strong material results, which may therefore be made with thin walls, and correspondingly more elastic and more efficient in cooling action. For mere storage, with no temperature changes, the vessel walls are made thicker. For further information will be found in Chapter 10.

Hard Rubber. Hard rubber piping, pumps, and pistons have been used with success in a number of cases; as example, hydrochloric acid can be pumped from one place to another one-quarter mile away by means of a small hard-rubber power pump and hard-rubber piping. Hard rubber can be threaded, and the threaded pipes put together with unions and nuts; still another advantage is that hard rubber may be softened by steam. It remains unattacked by almost any acid; hydrofluoric acid does not attack it.

Rubber-lined steel tanks for pickling, rubber-lined car tanks for hydrochloric acid, and rubber-lined pipes and fittings are widely used and absolutely reliable. *Vulcalock*, for example, is a multilayer lining which unites steel and rubber. It is built up from the metal wall with rubber cements, rubber sheets, hard rubber sheets, and again a multiplicity of soft rubber sheets, to a thickness of $\frac{1}{4}$ inch or so. The bond to the metal is perfect. A brick lining may be installed to protect the rubber for certain

Duriron. Duriron is a cast iron with abnormally high silicon content, about 14 per cent; it is practically unaffected by sulfuric or nitric acids, and only very slightly by hydrochloric acid. The drain pipes from sinks in chemical laboratories are made of Duriron, which resists completely the action of dilute solutions of all kinds of chemicals. Generally the bleacher in a nitric acid plant is made of Duriron, for this material has the passivity of stoneware combined with almost the strength of cast iron, and a thermal conductivity surpassing that of stoneware and approaching that of cast iron. Acid lines are frequently Duriron, and in general, this alloy is a boon to the chemical industries. Tantiron and Corrosiron are chemically similar high-silicon cast irons, and serve similar purposes.

Duriron is extremely hard and brittle; it must be reinforced in many cases by a cast iron or steel envelope or frame. Duriron cannot be welded, drilled, or threaded; in order to face two flanges so that they can be joined, they must be ground with abrasives, a tedious and expensive process.

Nickel Metal. This white metal contains 67 per cent nickel, 28 per cent copper, and 5 per cent other metals, but no zinc, tin, nor antimony. It melts at 2480° F. (1360° C.), higher than cast iron or copper (specific

gravity 8.87 cast). It is unaffected by common salt solution, while cast iron, steel, and copper are attacked. With many other chemicals it is comparatively inert, although it does not resist acids as well as duriron does, but monel metal has the great advantage that it can be drilled and tapped, and in general handled in the machine shop as steel is. It may also be cast. The tensile strength of monel metal is greater than that of mild steel and equal to that of medium steel.⁴

Monel metal may be drawn into wire, and the wire woven into cloth which may be used in the filtration of alkaline slurries. Iron wire cloth is used for the same purpose, but is less durable.

Monel metal is much more expensive than iron or steel, but in spite of this, its use has been expanding. Rotary driers for salt (NaCl) (55 feet long, 6 feet in diameter, for example) have been lined with monel metal plates, held in place by bolts of the same material. In refrigeration plants, all parts which come in contact with the brine give better service if made of monel metal. For the handling of sea water (on board ships) it is made into pump linings and pump rods; propellers of all sizes have been made of monel metal.

Chromium Alloys. Chromium steel and iron find several important applications in the appliances of the chemical engineer. The alloy consisting of iron and 13 per cent chromium resists the corrosion of water, salt water, and a great number of other liquids; it is often called stainless

TABLE 91.—Composition and corrosion-resistance of some chromium alloys.

Alloy	Composition	Resists
Allegheny metal	Fe; Cr 17-20; Ni 7-10; Mn <.5; S <.5; C <.2	H ₂ S, SO ₂ , oxides of N, HNO ₃ , NaOH, NH ₄ OH
Duriron (not machinable)	Fe; Si 14.5; C .85; Mn .35	H ₂ SO ₄ , HCl, HNO ₃ , HAc, NaOH, NH ₄ OH, Cl in Aq. sol.
Elcomet K	Ni 22; Cr 23; Cu 3.5; Mo 2; W .13; Fe 48; Si 1.25; Mn .50; C .12	Corrosive mine waters in coal mines; any acid liquor.
R-55 (La Bour)	Ni 52; Cr 23; Cu 6; Mo 4; W 2; Fe 8; Si 4; Mn .50; C .25	Viscose solution in rayon plants.
Hastelloy A	Ni 60; Fe 20; Mo 20	Dil. cold H ₂ SO ₄ , dil cold HCl, HAc, NaOH NH ₄ OH
Nichrome	Ni 60; Fe 25; Cr 15	
Stainless A	Fe; Cr 14; C .35	HNO ₃ , HAc, NaOH, NH ₄ OH
Stainless N	Fe; Cr 18; Ni 8; C .18	HNO ₃ , HAc, NaOH, NH ₄ OH
Stainless steels	Fe; Cr 8 and over; Mn 4; C <.12	HNO ₃ , HAc, NaOH, NH ₄ OH
Stellite (not machinable).	Co 40-80; Ni 0.25; Cr 20-35; C .75-2.5	H ₂ SO ₄ , HAc (in absence of air), NaOH
Monel metal	Ni 60-70; Cu 25-35; Fe 1-3; Mn .25-2; C .5-3	SO ₃ , NaOH, HCl, H ₂ Si
Zirconium #200	Zr 2.77; Si 9.15; Ni 71.41; Al .32; Fe 12.03	

⁴ For tensile strength of steel, see Chapter 48; monel metal has 90,000 pounds per square inch tests on rods (booklet on Monel Metal, by the International Nickel Co., New York).

4. It serves in the form of pipes, valves, autoclaves, and other containing vessels, also in making cutlery. As an example of the wide range of possibilities, it might be stated that the 14 per cent chromium alloy with 0.15 per cent carbon resists nitric acid of any concentration at any temperature below the boiling point; it has been found suitable as the structural material for reaction and absorption towers in the ammonia liquefaction process.⁵

Not only the chromium-iron alloys, but chrome-plated steels are very resistant to corrosion, so that chrome plated pieces of large sizes are now made by the chemical engineer. As example, the vaporizing chamber in the Dubbs process for cracking oil for gasoline might be given. Plated stoneware and automobile fixtures are very beautiful, with a high luster and bluish color; they do not tarnish. A number of alloys are described in Tables 91 and 92.

TABLE 92.—Corrosion tests on special material for comparison with zirconium alloys.¹

Sample	C* in 5 per cent HCl Aërated	C in 95 per cent H ₂ SO ₄
Duriron	0.00002
Cast steel	0.04468	0.00817
Cast iron	0.16298	0.00004
Hastelloy A	0.00437	0.00001
Zirconium, #200	0.00366	0.00006

Taken from "Corrosion resistance of zirconium alloys," H. L. Coles and J. R. Withrow, *Trans. Inst. Chem. Eng.*, 27, 253 (1931).
C = Corrosion expressed as inches penetration per month.

Fused Silica. A material totally unaffected by acid gases is fused silica, available in many forms, among others in 4-inch diameter S-bends, suitable for the cooling of hydrogen chloride. Other shapes are recommended for absorbers of the same gas in water. Silica pipes withstand changes of temperature better than stoneware, and are used for a first cooler (in the Mann process) with good results, but otherwise its service is not markedly superior to that of stoneware, which is far cheaper. Silica is furthermore easily broken by an accidental blow.

For the preparation of chemically pure water, a silica apparatus is well adapted.

Pyrex Glass by itself, and not merely as a lining, is fast taking an important place among the materials available to the chemical engineer. For example an all "Pyrex" distilling column, about 20 feet high, is available, and offers the advantage of permitting the observer to follow the distillations. The bells on the several plates are fastened down with "Pyrex" washers and nuts.

Glass-lined cast-iron vessels combine the inertness of glass with the strength of cast iron; they are used for numerous evaporations and reactions. For the preparation of yeast cultures brass-lined tanks are indis-

¹ An electronic theory for the development of passivity in a chromium-iron alloy for example states that an electron in the "s" level of the iron migrates to the available "d" level, which can accommodate five electrons of the chromium atoms, and that this adjustment is the cause of passivity or lack thereof. The theory permits an estimation of the amount of alloying element the iron should have, and the estimate agrees closely with the alloys used in practice. "The nature of passivity in stainless steels and other alloys," parts I and II, by H. H. Uhlig and J. Wulff, *Amer. Inst. Met. Eng.*, 135, 494 (1939); part III, by H. H. Uhlig, *ibid.*, 140, 387 (1940).

pensable. For many purposes, fair-sized enameled and glazed porcelain vessels may be improvised from slightly defective (in shape) bathtubs, rejected for the regular trade.

Sulfur-containing cements, melting at a moderate temperature, may be flowed over the inside of a cast-iron vessel coating its walls, so that it becomes acid-resisting, for cold acids (basolite).

A material called *Mammut*, of German origin, has become of importance in the wineries, for coating the inside of wooden tanks as well as concrete ones, in which the grape juice and the fermented product is held. *Mammut* is black, resembles wax in appearance, is tasteless, almost odorless, and insoluble in the dilute alcoholic and acetic wine solution. The faint odor which it has is that of an odoriferous balsam.

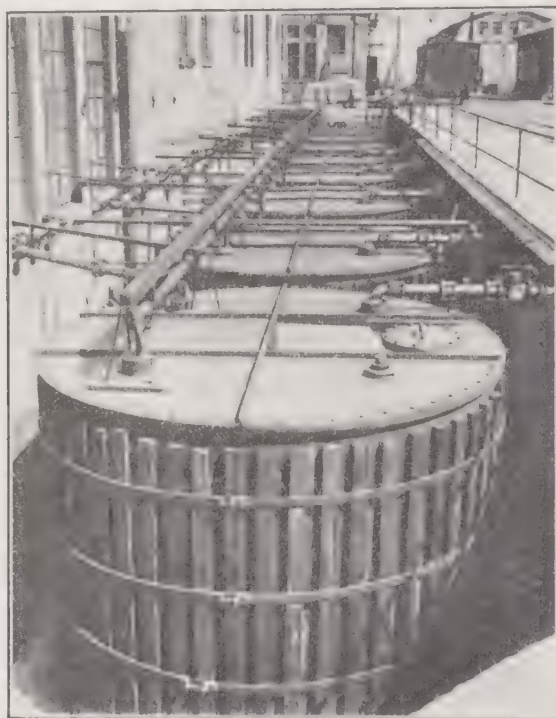


FIGURE 262.—Storage tanks for 40 per cent hydrochloric acid made of Haveg, reinforced by outside wooden strips. (From the Bergius plant for Wood Hydrolysis, Heidelberg.)

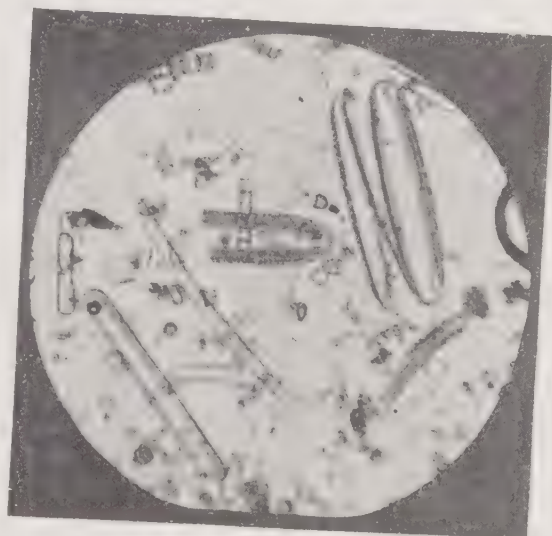
The structural material Haveg consists of a phenol-formaldehyde resin containing a selected asbestos filler. It is a strong material, and has the particular merit of resisting most acids of low and medium concentrations. Specific gravity, 1.6; compressive strength 10,400 lbs./sq. in.; unchanged in any way up to 130°C . (265°F .). It has a low heat conductivity. Haveg is made into tanks 10 feet high and 10 feet in diameter. Tanks for pickling iron, for electrolytic processes, for dyeing operations, are available of Haveg. In many cases, a steel shape is covered with the resin and filler, combining the strength of steel with the inertness of the resin. Haveg does not resist acetone, strong oxidizers, pyridine, or sodium hydroxides.

Tower Packing. For the absorption of gases in water, towers may be packed with coke, an inexpensive packing. Broken stoneware may be used or "rings," short cylindrical pieces of any desired diameter and of any material.

stoneware, Duriron or other. For sulfuric acid, quartz lumps, with regular shapes, and classified as to size, are used. Hollow spheres of stoneware have been proposed, while the so-called spiral chemical rings, in two sizes, 6 and 3 inches in diameter, have been very successful.⁶ A good pack must offer maximum surface of the liquid to the gas, retain the descending liquid for a period long enough for saturation, and allow free circulation of the ascending gas. The Berl saddles excel in this respect; they are made of stoneware, porcelain, or other material.

Catalysts and adsorbents are discussed in their proper place in other chapters. The science of catalysis is rapidly advancing, but as yet many chemists must make their own catalysts, because some of the catalysts are not as such on the market, even in a preliminary form. As adsorbents, coal and silica gel are best known; both have been applied to the

FIGURE 263.—Diatomaceous earth, from New York State, showing the fine structure which gives rise to large surface; run of unselected sample. Micrograph as reproduced, 62 diameters. (Photographed in author's laboratory.)



adsorption of valuable gasoline vapors from natural gas. Silica gel is made⁷ from silicate of soda solution (sp. gr. 1.185) by the action of hydrochloric acid (10 per cent), at the temperature of 50° C., with stirring. After setting, the gel is washed free from salt with water and dried in a current of air at 75° to 100° C.; finally heated in a vacuum. Hard, transparent, granules result, with high adsorptive power. The gel is stable to heat. Only by observing certain definite conditions is the gel obtained in a stable form, with high commercial value. Activated alumina is a partially hydrated aluminum trihydrate, which can adsorb as much as 14 per cent of its weight in gases and vapors. As for silica gel, the alumina must be reactivated by heating, to 350° to 600° F., followed by cooling before starting the next cycle. Activated alumina is furnished in granules which pass an 8 to 14 mesh, and other sizes. Silica gel is furnished in a similar size granule, and also, for certain adsorptions, in powder

⁷ Manufactured by the B. Miffin Hood Brick Co., Atlanta, Ga. Patent 1,297,724 (1919), to Walter Patrick.

Aids in filtration in the form of fine powders, usually natural powders, such as diatomaceous earth, have been introduced under various names (Silocel) and have proved of great help; they are stirred into the turbid liquid, and after some time the filtration is performed. The very fine, essentially colloidal particles of the turbidity are adsorbed by the added powder. The same powder frequently removes color as well as turbidity, but not always; with oils, such as linseed oil and also wood-tar oils, fuller's earth (a clay) has reduced color.

Decolorizing agents include "chars," which were made originally by charring bone; the residual carbon is accompanied by a calcium phosphate substructure. In using these decolorizing agents, they are added and suspended in the solution to be cleared of color; after some time, the suspension is filtered. For acid solutions, bone char is objectionable, as some phosphoric acid forms. The "vegetable chars" and specially trade-marked articles do not contain phosphates. One of them is carbon with 40 per cent fine sand which passes a 200 mesh sieve; the presence of the sand facilitates the suspension, and especially renders the subsequent filtration easy and rapid.

Plates for the filtration of very acid solutions, such as concentrated sulfuric acid, consisting of porous silica ware, have been received with favor (Filtros). A single plate is perhaps 10 by 10 inches; if a larger surface is desired, several plates are set in an acid-proof cement to form the roof of a box, to which suction may be applied to facilitate the filtration.

SHIPPING CONTAINERS

The mineral acids were shipped in former days in glass carboys of the balloon type, packed in hay or ground cork. For nitric acid, such packings are dangerous, and the Stahl carboy was developed, in which a 12-gallon bottle with straight sides is held in place by four strips of wood at the corners of the containing box; the surface of the strips (4 inches wide) is grooved to soften it. The dimensions of the box and of the bottle are so adjusted that the bottle can just be forced in place by gentle pressure. This style carboy was so successful that it has become standard for all acids.

Glass- and lead-lined containers were used exclusively for the shipment of sulfuric acid until steel tanks, portable and stationary, were introduced. This simplified the shipping of sulfuric acid and mixed acids, reducing the labor cost and the loss due to breakage; it took some time to convince customers that acid shipped in steel drums holding 2000 pounds or steel tank cars holding twenty times as much was as good as acid shipped in the familiar glass carboys.⁸

Single tanks on a railroad flat car, used for many years only for crude oil and petroleum products, have gradually become standard in nearly all branches of chemical manufacturing. Steel for sulfuric acid and mixed

⁸ Dr. Wm. H. Nichols said: "The first change from the carboys to iron or steel for sulfuric acid containers was a cylinder placed on a barge, capable of holding 50 tons of product. One small reformer was induced to put in a steel receiving tank, but for one whole year, a second one equally dangerous could not be found. It was feared not only that the acid would eat the container, and destroy it, but also that the acid itself would become weak." *Ind. Eng. Chem.*, 10, 768 (1918).

is well known. Anhydrous ammonia is shipped in car tanks of similar single units for liquid sulfur dioxide, and for liquid chlorine, are in use. A tank of aluminum for 98 per cent acetic acid has been adopted well suited. Steel tanks with a thin nickel lining have been introduced. Light sheet-steel drums with tight covers are much used, also steel keels, tight wooden barrels for liquids, sometimes paraffin-lined. Square boxes in wooden protecting cases are used for hydrofluoric acid, also sine bottles. Mercury is transported in cast-iron flasks. Many solids shipped in bulk, or in sugar barrels (not air-tight). There is promise at the present time that a drum of light weight with welded joints will be developed, of chrome-iron alloy (17 per cent Cr), in which nitric acid made by the oxidation of direct synthetic ammonia, hence free from halogens, may be shipped. Tank cars of the same material suitable for such nitric acids are now constructed. Welded steel barrels and drums are being developed especially for the brewery trade.

OTHER PATENTS

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For the control of operations in industrial plants, the chemical engineer at his disposal a fast-growing array of instruments; their relative values best exhibited by grouping them together in one discussion.

Chapter 46

Instruments of Control Used by the Chemical Engineer

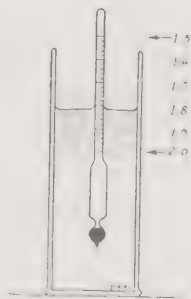
HYDROMETERS

The concentration of a solution, for instance of sodium thiosulfate, is varied to proceed until the density reaches a definite point, which trials have shown to be high enough so that on cooling a rich crop of crystals will be formed, yet low enough to contain enough water to form a mother liquor which will carry away the impurities; that density, in this case 51° Bé. The hot liquor, is determined by means of a hydrometer. In countless other similar preparations of liquors, similar tests are made with the help of the same instrument.

In the manufacture of sulfuric acid by the chamber process, the amount of steam or sprayed water sent into a chamber depends upon the strength of the acid drips; this strength is determined by the hydrometer. For the process of dilution or of strengthening of this acid, and many others, the same instrument is used.

The simplicity of the apparatus needed insures its continued use; a container, usually a glass or lead cylinder, the hydrometer proper, and a thermometer, form a complete set.

FIGURE 264.—Hydrometer for liquids heavier than water, for the range in specific gravity of 1.500 to 2.000.



Hydrometers for Liquids Heavier than Water. A hydrometer is a float, a lower wide chamber which is suitably loaded with mercury or iron shot, and an upper tubular chamber in which a scale is provided. The float is buoyed up to a height depending upon the specific gravity of the liquor; the higher the specific gravity, the higher is the float pushed up. The point on the scale on a level with the surface of the liquid, after the instrument has come to rest, is read. The construction of the hydrometer is shown in Figure 264.

The "common" hydrometer reads from 0° to 72° Bé., and frequently also the equivalent metric values, the specific gravities, from 1.000 to

2,000. The smallest division is one whole degree, and can hardly be subdivided; this instrument is therefore used for the first approximation, indicating which one of the finer ones should be used next. A scale of degrees Baumé forms usually one instrument of the more accurate type, each degree being subdivided into tenths; these are wide enough to allow an estimate to within 0.02° Bé., equivalent to about 0.005 on the metric specific gravity scale. Hydrometers graduated for specific gravity readings are coming into use more and more; for the finer types, the scale covers one-tenth (thus 1.200 to 1.300), subdivided in ten hundredths, and each of these in ten thousandths; each of these last divisions may be subdivided by estimation into fifths, giving a final reading to within 0.0002 on the metric specific gravity scale. Thus for the space from 1.000 to 2.000 there would be ten glasses; such glasses are usually kept in the plant laboratory and the samples to be tested are brought there.

In order to insure accuracy to the last estimated place, a set of glasses standardized at the Bureau of Standards in Washington is kept in the laboratory for comparison only; a second set, the one in use, is compared with the standards and the necessary corrections listed on the cover of the containing box.

Temperature Corrections. Such accurate hydrometers would have no meaning if at the same time the temperature were not determined; this is usually done by means of the same instruments, which carry an enclosed thermometer reading from -10° to 40° C. or the corresponding values in the Fahrenheit scale. By means of tables, or in the absence of tables by means of determinations, a correction for temperature is applied, in order to reduce the readings to 60° F., the standard temperature.

For example, a sample of muriatic acid gave the reading of 21.6° Bé. at 74° F.; the correction for the range 22° to 25° Bé. is one-twenty-eight degree Bé. to be added² for each degree Fahrenheit over 60° ; hence

original reading	21.6
correction for error of scale0
correction for temperature $1/28 \times 14$5
	<hr/> 22.1

As the acid must be 22° Bé., in this case, it just passes.

Using metric specific gravities the corresponding values would be:

original reading	1.1751
correction for error of scale	0
correction for temperature 0.00035×140049
	<hr/> 1.1800

For control within the plant, the accuracy is not so great; a liberal margin of safety is provided by making the goods intended for shipment distinctly overstrength.

The relation between the Baumé scale and the metric specific gravity

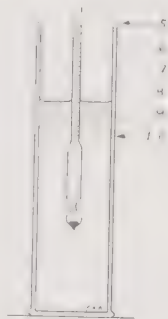
¹ Such standard sets are usually the pride of the laboratory.

² For temperatures above 60° F. the correction is added; below 60° F., subtracted. 60° F. = 15.56° C.

le and a table for the Baumé scale for liquids heavier than water with the corresponding specific gravities is given in the Appendix.

Hydrometers for Liquids Lighter than Water. A water solution of ammonia decreases in specific gravity as its content of ammonia increases; the strength of the liquor is judged in this case also by means of a hydrometer which must be graduated in such a way that the further it sinks in the liquid, the higher will be the reading in degrees Baumé on the scale. This is therefore an entirely different Baumé scale, which is distinguished from the previous one by adding the words "for liquids lighter than water." The

FIGURE 265.—Hydrometer for liquids lighter than water, for the range in specific gravity of 0.500 to 1.000.



corresponding specific gravities are less than unity. Such an instrument is shown in Fig. 265. A table giving the Baumé scale for liquids lighter than water with the corresponding specific gravities will be found in the Appendix.

A correction for temperature differing for each liquid must be applied; for temperatures above 60° F., it is subtracted.

TEMPERATURE MEASUREMENTS

For temperatures between -20° C. (-4° F.) and 360° C. (680° F.), an ordinary mercury thermometer is used widely, in spite of the fragility of the glass container. Such an instrument is really a dilatometer; the expansion of the mercury at the various temperatures is measured against a glass scale. A nitrogen-filled mercury thermometer will read temperatures to 550° C. (1022° F.); such instruments are made of special, hard glass, which fuses only at still higher temperatures.

Pressure thermometers, which may be gas-filled, vapor-filled, or liquid-filled, are widely used, and are comparatively simple instruments. The pressure developed in the vapor tube, for example, distorts a Bourdon gauge; the reading of the pressure becomes the measure of the temperature. The application of the hand is also a practical method for judging moderate temperatures.

Thermocouples are used over practically all ranges of temperatures from that of liquid air (-190° C., -310° F.), to 1400° C. (2552° F.), which is the heat of a coal fire under forced draft. For temperatures between 0° C. (32° F.) and 1000° C. (1832° F.), resistance pyrometers, especially platinum ones, are valuable. For temperatures above 1000° C., in addition to thermocouples, radiation pyrometers, optical pyrometers, and

Seger cones are used in industrial plants. These instruments may each be used over wider limits than indicated. The choice of instrument will depend not only upon its special adaptability for the temperature range to be studied, but also upon the danger of deterioration if immersion in a fusing chemical for instance is required; the radiation and optical pyrometers would then be preferred as they have the advantage of being operated at a distance from the furnace or hot object.

A single observation may be required once in a while, or regular observations at stated intervals, or constant readings; the latter are now made from charts marked by recording pyrometers, on which not only the high and low points appear, but the temperature at every moment.

Thermocouples. When two dissimilar metal wires are joined in two places and one junction is heated while the other one remains cold, an electromotive force is set up in the system which is a function of the temperature at the hot junction, provided the cold junction remains at an even temperature. (See Fig. 266.) Such pairs of wires are chosen as will remain



FIGURE 266.—Diagrammatic sketch of a thermocouple with millivoltmeter.

unaltered at the temperatures to be measured, and if several pairs are suitable, that pair is selected which gives the greatest increase in electromotive force for each degree rise; a third criterion, and not the least important, is the cost of the metals.

The electromotive force is measured on a millivoltmeter³ which may be graduated in millivolts, or directly in degrees; if in millivolts, the degree corresponding to each reading is read off on a chart, on which the temperatures are entered as abscissæ, the millivolts as ordinates; for each thermocouple a separate chart is made by reading the electromotive force set up in two or more baths, or regions, of known temperatures; if graduated in degrees, a certain voltmeter must be used for a designated thermocouple, and the reading is direct.

The instrument in its simplest form is portable, and consists of the fire-end, which is the thermocouple proper, sheathed in an iron or porcelain protecting tube; two copper leads, and the millivoltmeter.

The electromotive force may also be measured by means of a portable potentiometer, in which the electromotive force set up in the thermocouple is matched by an oppositely directed electromotive force until a galvanometer needle shows zero current. Dry cells may be used for the matching current, and compared daily to a standard cell, such as the Weston. The potentiometer system for thermocouple currents is coming into increasing favor; it is a little more complex than the millivoltmeter method, but more than the platinum resistance pyrometer. It consists of the fire-end, the thermocouple proper, the copper leads, and the potentiometer box con-

³ With high or low internal resistance; the high internal resistance type has the advantage in that even considerable variation in the leads has no effect on the reading.

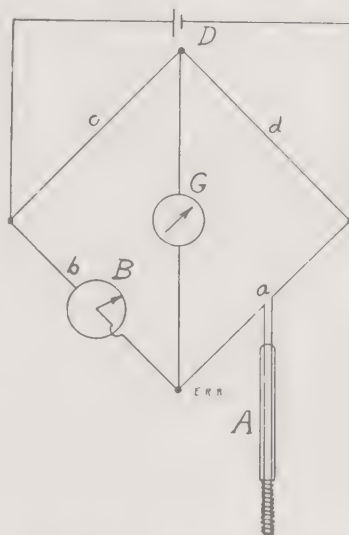
ing a cell, slide wire, and zero point galvanometer. The length of the drum-wound slide wire turned into the circuit is the measure of the match-current. Automatic potentiometers which are also generally recording, are based on various principles such as slide wire, photoelectricity, and a combination of the two, are in very general use.

For precision work, in the laboratory, the cold junction which is here binding post at the exit of the wires from the fire-end, is placed in an ice bath; in the plant, the temperature of the room is constant enough. The smaller the difference in the temperatures of the two junctions, the less does it matter whether the room temperature is constant or varies somewhat; but in this respect, high temperatures will be more accurately read.

The following pairs are suitable for the temperatures listed opposite them:

Silver—constantan	room temperature up to 500° C.
Copper—constantan	" " " " 700° C.
Iron—constantan	" " " " 1000° C.
Chromel—alumel	" " " " 1000° C.
Platinum—platinum + 10% rhodium alloy	" " " " 1400° C.
" " " " " " " " " " " "	for short periods to 1500° C.

FIGURE 267.—The platinum resistance pyrometer. *A* is the fire-end, forming arm *a* of a Wheatstone bridge; *B* is the drum-wound slide-wire, forming arm *b*; *c* and *d* are the other two arms, which consist of fixed resistances; *G* is the zero galvanometer; *D* is the dry cell used for intermittent readings.



constantan¹ contains 60 per cent copper and 40 per cent nickel; chromel, 90 per cent nickel and 10 per cent copper; alumel, 98 per cent nickel and 2 per cent copper. The alloy platinum-iridium is also used instead of platinum-rhodium.

The relative sensitivity is indicated by the figures in the table below:

	E.m.f. in Millivolts	
	at 500° C.	at 1500° C.
Copper—constantan	27.8	...
Silver—constantan	27.6	...
Iron—constantan	26.7	...
Chromel—alumel	20.8	...
Platinum—platinum + rhodium alloy	4.4	15.1

¹ named because its electrical resistance is practically constant over a wide range of temperatures.

Resistance Pyrometer. The resistance of a coil of platinum varies with the temperature; this property is the principle of the resistance pyrometer. The coil is made one of the four arms of a Wheatstone bridge; a slide-wire, drum-wound, is adjusted so that the needle of a galvanometer shows no deflection; the length of wire needed for this adjustment is the measure of the temperature. The reading is direct, as the scale is graduated in degrees. The arrangement is shown in Figure 267.

The platinum resistance pyrometer is not as rugged as the thermocouple; it is also slower in response. If it is fixed in the region to be measured and not removed except for shutdowns, it is a reliable instrument and will give many years service. It is best suited for temperatures below 900°C .; for instance for the mechanical salt-cake furnaces, it has proved itself well adapted.



FIGURE 268.—The Radiamatic, an example of the radiation pyrometer, showing the collecting lens and conduit connections. (Courtesy Brown Instrument Company, Philadelphia, Pa.)

Radiation Pyrometer. The radiation pyrometer receives heat radiations from a furnace or hot body⁵ through a collecting lens which focuses them on a very small thermopile. The current generated is measured by means of a potentiometer, hand operated or automatic. The cold junction is screened from heat radiations. The radiation tube may be held in the hand or it may be mounted in a fixed position. The radiation pyrometer has been gaining over other instruments because none of its parts need to be inserted in the hot chamber, fluid or wall, with its attendant damage.

The Radiamatic for intermediate range measures temperatures up to 2300°F . (1260°C .), and has a silica lens. The high-range Radiamatic

⁵ A "black body" absorbs all incident radiations, transmits none, and itself radiates as fast as it absorbs.

measures temperatures between 2300 and 3200° F. (1760° C.) and higher, and has a Pyrex lens. The target diameter should not be less than one twentieth of the distance between the lens and the object.

Optical Pyrometer.⁶ The optical pyrometer shares with the radiation pyrometer the great advantage of not requiring introduction into the bath region to be measured. The inner wall of a window-glass melting pot, for instance, is sighted through the instrument; in the field of vision a platinum loop is placed. The loop may be heated to dull red, bright red, or white, by sending a varying quantity of current from a dry cell through it. Just so much current is sent through as needed for exact matching of the field, when the wire loop cannot be seen at all; a little more current and the loop appears, and is whiter than the field; a little less and it appears gray, but darker than the field. The reading for a perfect match is readily duplicated by different observers to within 4° C. near 1400° C.

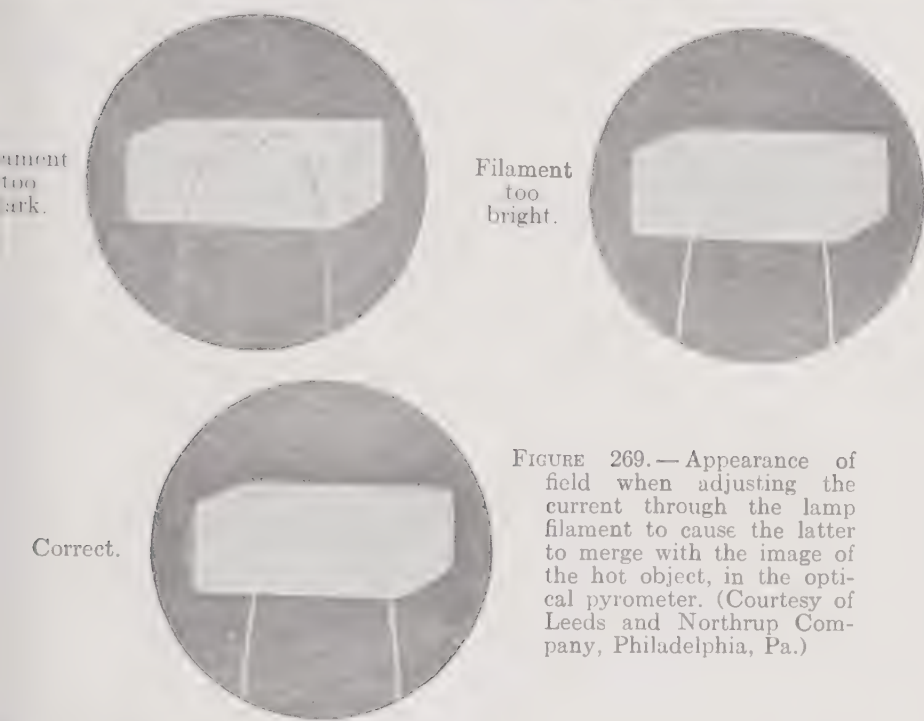


FIGURE 269.—Appearance of field when adjusting the current through the lamp filament to cause the latter to merge with the image of the hot object, in the optical pyrometer. (Courtesy of Leeds and Northrup Company, Philadelphia, Pa.)

The complete apparatus consists of the sighting tube containing the filament lamp, a storage battery, a rheostat, and a milliammeter. Its field of usefulness lies from temperatures corresponding to dull red, about 600° C., to temperatures higher than correspond to white heat.

Instruments procured from the dealers are ready for use, and are usually put into service without further testing. Should any doubt arise as to correctness of the reading, the instrument may be sent to the Bureau of Standards at Washington, for certification. The standardization may be done in the laboratory of the plant if enough time is allowed to acquire the

Optical pyrometers are radiation pyrometers limited to visible radiations.

necessary technique, for it is specialized work, and very misleading figure may be obtained. The fixed points recommended are:

Melting point of	Zinc	419° C.
"	" Aluminum	657
"	" Silver	961
"	" Gold	1063
"	" Nickel	1452
"	" Palladium	1549

The most reliable method of testing a thermocouple for the gold melting point for instance, would be to separate the wires at the fire-end junction (hot junction) and place a short piece of gold wire between them making good electrical contact; the rest of the apparatus would be as usual. On heating the fire-end slowly at a definite rate and watching the millivoltmeter, there will occur an interruption to the gradual rise of the needle and a sudden return to zero; the maximum reading made will correspond to the melting point of the gold. At least two such points are tested and the curve drawn for the intermediate temperatures.

The comparison of two different pyrometers is another way to standardize; for instance, a radiation pyrometer may be sighted on the fire-end of a platinum-platinum rhodium thermocouple; or two thermocouples may be placed side by side. Sufficient time must be allowed for both instruments to reach their maximum reading, and the means of three trials is taken.

Pyrometric Cones. Pyrometric cones, formerly called Seger cones, are really slender triangular pyramids and are made of mixtures with definite fusion points. (See Fig. 270.) They are used in groups of three, numbered



FIGURE 270.—Pyrometric cones.

for instance 9, 10, and 11, set close together in a small lump of clay; the group is pushed into a porcelain kiln, as example, within range of a peephole. The firing will be increased until No. 9 melts and bends over completely, No. 10 softens enough to have its tip leaning over; No. 11 is still erect. If the firing is now maintained constant, or decreased, so that No. 11 remains unaffected, the maximum temperature which has been reached is that corresponding to No. 10, namely, 1305° C.; that corresponding to No. 9 has been exceeded, 1285° C., while that temperature corresponding to No. 11 has not been reached, 1325° C. It may be said that the temperature reached is determined to within 20° C.; this is not quite certain, but the observation of the cone may be made finer in this way: It is observed that the upper half of the cone leans over, the lower half is erect; that point is taken to be exactly 1305° C.; if only the upper third leans over, the temperature is about 1295° C.; if the lower half has started to lean over, the temperature is about 1315° C.; hence the accuracy may easily be said to be within 10° C. By making intermediate cones, the limit may be narrowed to 5° C.

less; the commercially obtained cones are made for 10° to 20° C. intervals, as that is close enough for ordinary operation in many industries. They are inexpensive, which is essential, as they are used but once.

For the range 1160° to 1810° C. Nos. 1 to 36 are made, leaving a difference of 10° to 20° between any two; the materials are feldspar, marble, quartz, and kaolin in varying proportions; No. 1 has 83 per cent feldspar, and only a trace of kaolin; whereas No. 36 has no feldspar, and all kaolin. The most widely used cones are Nos. 1 to 12, 1160° C. to 1335° C. Another series of ten numbers registers over a range of 895° C. to 1145° C.; and still another between 605° to 875° C. (Chapter 10).

Potteries are the plants in which pyrometric cones were chiefly in use; they still are, but of late the recording thermocouple pyrometer has been introduced. The cones will continue in use, however, where the accuracy of the temperature indication which they give is sufficient for the control of the operation. If a fluctuation of 20° C. does not matter, it is a waste of effort to make measurements within 4° C. The pyrometric cones suffer from all indicating instruments do, from the fact that they do not give information on how long a certain temperature was maintained; this is done only by the recording pyrometers.

Thermal Conductivity Cell for Gases. Supplementing chemical methods for gas analysis, the thermal conductivity of gases has been made the basis of a method of analysis⁸; heat enters the gas through platinum spirals which receive a measured current. The heat conductivity values which now will indicate the applicability of the cell:

Air	1.00	Ammonia	0.81
Hydrogen	7.35	Methanol gas	1.31
Carbon dioxide	0.58	Nitrogen	1.00
Sulfur dioxide	0.41	Oxygen	1.00

The cell for thermal analysis of carbon dioxide containing gases as manufactured by the Brown Instrument Company, may be taken as an example. Two gas wells are provided, through one of which (*O* in Figure 253), a portion of the gas to be analyzed is continuously bled, while the other (*P*) contains the comparison gas, air. In each cell there are 4 filaments (one not shown in figure); each pair forms one arm of a Wheatstone bridge. Hence two arms per cell, four arms for the two cells. A given current is passed through all filaments, heating them. Depending upon the thermal conductivity of the gas, heat leaks out to the metallic enclosing pipe, more or less fast. In the case of CO_2 , it leaks out less fast than for air. As a result, the filaments in *O* are hotter, their resistance is greater; the bridge is unbalanced. A different current is then able to flow, and this actuates heating and recording devices. A change in the composition of the gas is recorded in less than a minute.

In the *Ramaker analyzer*, which depends upon the density of the gases in its action, there are two chambers, each with a driven impeller which carries the gas forward; and each with a fan wheel which receives the driven

⁸As to analysis of gases, read "New forms of gas analysis apparatus," G. A. Burrell, *Ind. Eng. Chem.*, 4, 297 (1912). The simple Orsat apparatus is described in Chapter 12.

⁹"Electrical gas analysis for continuous processing," A. C. Schmid, *Chem. Met. Eng.*, 36, 230 (1929)

gas. Suitable outlets are provided for the gases. The impeller in chamber A runs clockwise. The fan wheel tends to rotate in obedience to the impulse from the gas. It cannot rotate, however, because it is connected by an outside rod to the fan wheel in the lower chamber; here, the arrangement is the same, but the direction of the driven impeller is counter-clockwise; hence, the impulse on the wheel in chamber B is opposite to that in A.

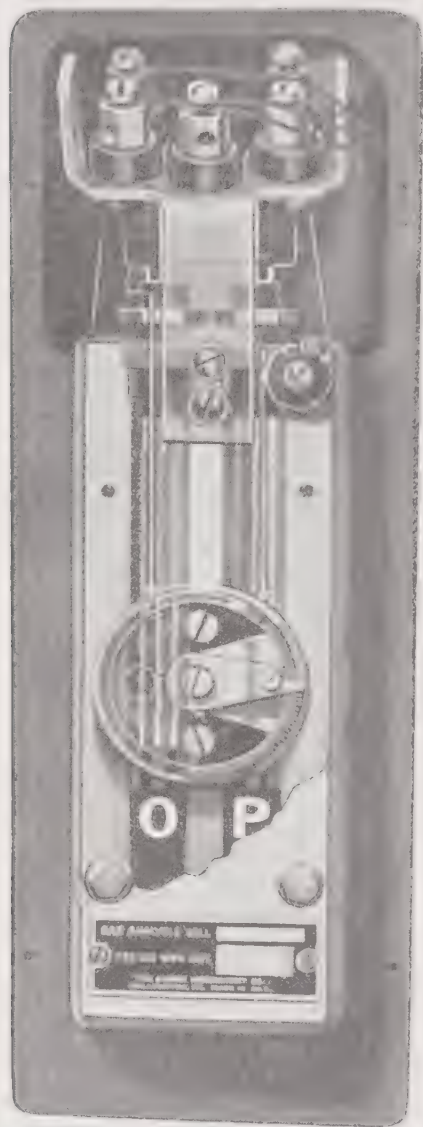


FIGURE 271.—Cell for thermal-electric analysis of a gas containing carbon dioxide; see text. (Courtesy of the Brown Instrument Company, Philadelphia, Pa.)

The same belt drives the two impellers. The rod which connects the registers the differential torque of the two fan wheels. If the gas in A is of the same density as that in B, the torque on wheel A will be equal and opposite the torque on wheel B, for the velocity given the gases are the same, and their densities do not differ. If the density of the gases differs, the torque differs, and there will be a movement of the rod toward one of

mm. away from the neutral position. This movement is magnified by means of levers and is transferred to a needle which travels over a scale. The Ramarex was devised primarily for flue gas analyses; the density of carbon dioxide is very different from that of air (as 44 is to 28.8) and a small percentage, more or less, has an effect on the torque of the wheels, when running on air. For ammonia-air mixture, it has been equally successful; here again the difference in densities is considerable (as 17 is to 28.8). For ammonia, the chambers are kept dehydrated by sulfuric acid; for flue gases, they are kept hydrated by water.^{8a}

AIR CONDITIONING

In many industries, such as paper, textiles, printing, it is necessary to regulate the amount of moisture contained in the air of the factory rooms, not only by maintaining a certain humidity, at a given temperature, but also the moisture-susceptible properties of the products be controlled. The "relative humidity" of the air is the ratio of water vapor actually contained in it to the maximum amount it may contain at that temperature. This maximum would be saturated air, whose relative humidity would be 100. It is important that the temperature at which a particular relative humidity is to be provided, be stated, for the same relative humidity at different temperatures stands for different absolute amounts of moisture. Thus, 40 relative humidity at 65° F. corresponds to 36 grains of moisture per pound of dry air, but 40 relative humidity at 85° F. corresponds to 72 grains of moisture, per pound of air.

The relative humidity is determined by means of two thermometers tied together; one thermometer bulb is left dry, the other is fitted with a wet cloth over its bulb. On placing these two thermometers, now termed a psychrometer, in the air to be tested, the wet bulb thermometer will register a lower temperature than the dry one. The differential will be greater the drier the air. From the temperatures, the relative humidity is read off on the chart (see Fig. 272), and applies to air at the temperature of the dry bulb thermometer. The absolute amount of moisture in grains, per pound of dry air, may also be found by means of the chart. With a sling psychrometer, the necessary equilibrium is attained in a minute.

Air conditioning means providing air with a definite, predetermined amount of water vapor, at a stated temperature. Partial humidification means the injection of atomized air in the rooms, in order to raise the moisture content. Complete humidification means either lowering, or raising of moisture content, as may be necessary. For the latter, as a rule, outside air is passed through a spray of circulated (and cooled) water at a low temperature; the air becomes saturated with moisture at the temperature of the spray. This may involve a cooling, and a deposition of water (dehumidification). Next the air passes baffles in order to deposit entrained droplets, and finally over steam coils in order to raise it to the temperature prescribed. There are many variations in procedure. In all, a fan pulls in new air, and delivers it to the ducts leading to the various rooms. Refrigeration and silica gel have been used for dehumidification.

^a The Permutit Company, New York.

The Cottrell electrical precipitator (described in chapter 43) has been applied to air conditioning. Its special efficacy is the removal of suspended solid particles below 5 microns in diameter, which are frequently of bacterial nature, and which escape the ordinary dry filter. The Westinghouse Electric and Manufacturing Company has announced (March 1937) a commercial Cottrell unit suitable for the home. The unit will follow the dry filter. The charged particles will pass between plates with a voltage

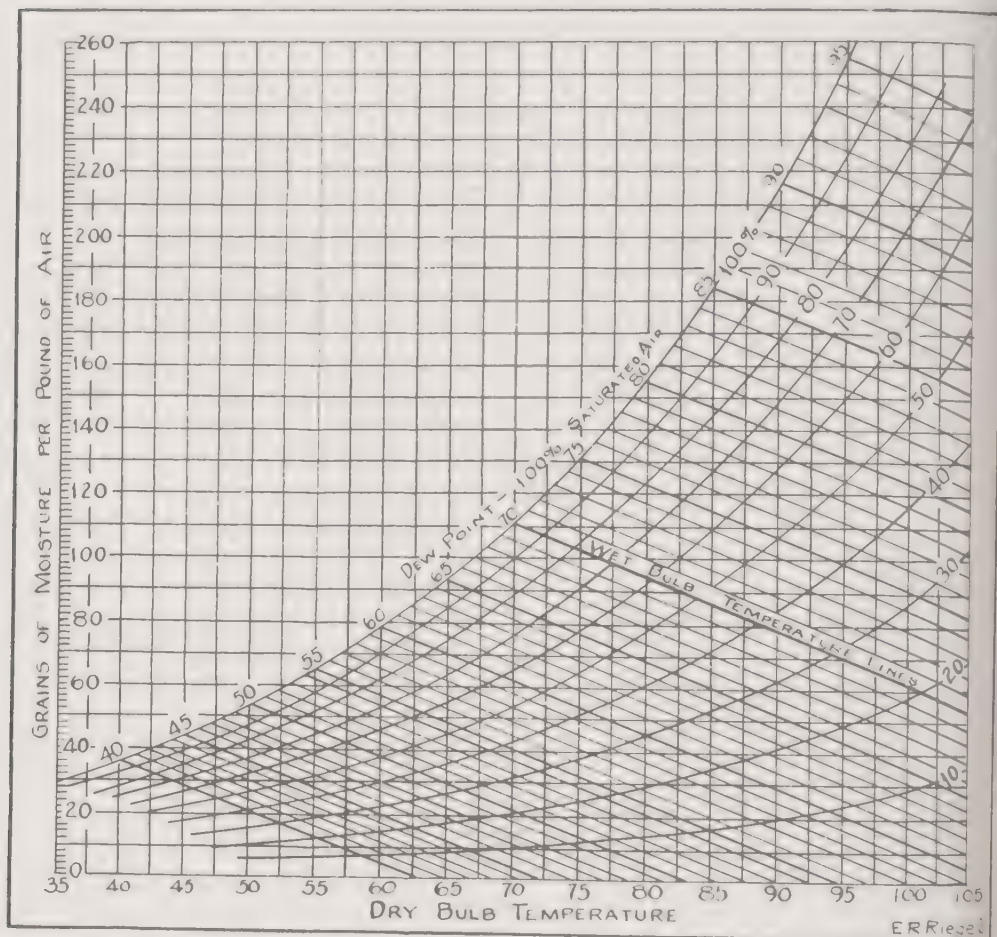


FIGURE 272.—Psychrometric chart, for determining the absolute and relative humidity in the air from wet and dry bulb thermometer readings. The curved lines are the relative humidities.

gradient of about 1400 volts per inch. All danger of ozone or nitric oxide formation is avoided by lowering the voltage to 15,000 from the original 60,000.

MEASUREMENT OF THE FLOW OF GASES AND LIQUIDS

The measurement of the flow of a gas or a liquid is a frequent operation; the quantity of a waste gas, sent up a chimney for instance, may be sought because of a certain content of a valuable gas or vapor; if the volume of gas passing out is known, an analysis giving the percentage by volume of

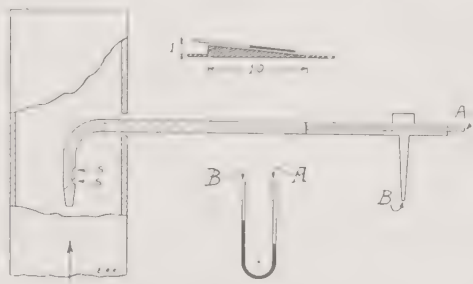
the valuable gas is all that is needed to make the calculation as to how much is lost per day.

The Pitot tube and the Venturi tube both measure velocity per second, and this multiplied by the area of the pipe gives cubic feet per second. An occasional measurement for which no installation has been provided is made by means of the Pitot tube; the Venturi tube is built into the line, and all the gas passes through it at all times.

Gas flow meters for small rates of flow may be constructed in the laboratory, and of glass.⁹

The Pitot Tube. The Pitot tube is a double tube, as indicated in Figure 273. One opening, facing upstream, receives velocity head and static head¹⁰ combined; a rubber tube transfers this double pressure to one leg

FIGURE 273.—A brass Pitot tube. *A* and *B* are connected to a vertical *U*-tube as indicated; for low velocities, the inclined manometer shown here is used.



a *U*-tube. Two small pin-hole openings permit the static pressure to pass through the outer chamber through a rubber connection to the other leg of the *U*-tube. In this way, the static pressure is eliminated in the reading; the difference in levels in the two legs of the *U*-tube is due to velocity pressure alone. The *U*-tube is filled with ether, or thin oil, or some other chosen liquid; for low velocities, the lightest liquid is used, ether, in order to obtain a large a reading as possible. The accuracy of the reading is increased by inclining the *U*-tube to near horizontal position, on slope of 10 to 1; this form is known as the Swan manometer. With the height expressed in terms of a vertical column of water, the formula $v = \sqrt{2gh}$ is used, usually with a factor of 0.9 to allow for the dragging effect of the pipe walls.

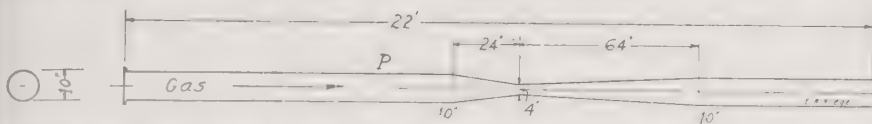


FIGURE 274.—The Venturi tube for measuring the flow of gases; a small pipe is soldered to the 4-inch throat, another at *P*, and connected to a *U*-tube.

Venturi Tube. If the normal diameter of a pipe be narrowed to form a throat, then flared out again to the original size, another means is provided to measure velocity. The relation between the diameters and the length of the constricted portions is approximately as indicated in Figure 274. The pressure at the throat will be lower than in the full-sized

⁹ *Ind. Eng. Chem.*, 11, 623 (1919).

¹⁰ The static head is the absolute pressure in the pipe.

pipe, if a gas is traveling through, and the difference between the two pressures, measured on a *U*-tube as before, is proportional to the velocity. In chemical plants, it is customary to standardize each Venturi tube by sending known volumes of air at various temperatures through it, and recording the readings. The theory is essentially the same as for the Pitot tube.

The Venturi tube may be vertical or horizontal, of lead or cast iron; the liquid in the *U*-tube is usually water, sometimes concentrated sulfuric acid, rarely mercury.

In the Thomas meter, for gases, essentially an electrical thermometer, a measured quantity of heat is furnished a traveling gas at a given point in the conduit; the increase in the temperature of the gas is inversely proportional to the quantity passing through per second; the more gas passes, the smaller the rise in temperature. A modern form of this valuable device is illustrated in Chapter 14.

In an *orifice flow meter*, a disk with a central opening, the orifice, is inserted in a pipe, constricting the flow of gas or liquid, and creating a differential in pressure. The pressure is higher upstream. The differential is applied to a mercury manometer, and its changes in level are read by means



FIGURE 275.—An orifice electric flow meter, indicating and recording. (Courtesy of the Brown Instrument Company, Philadelphia, Pa.)

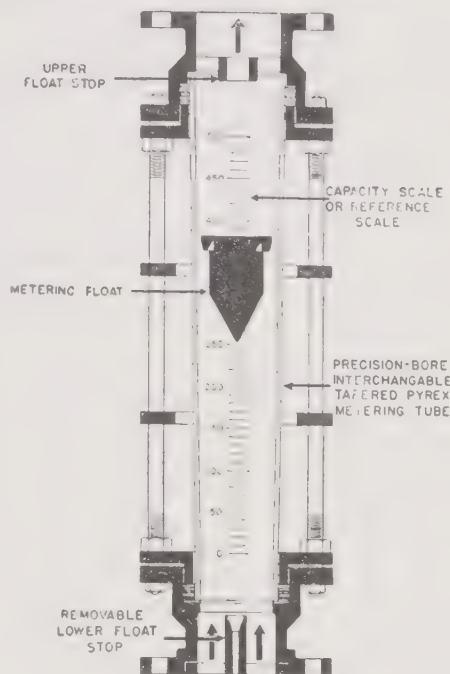
of a float, or electrically. In the brown Electric Flow Meter, the changes in level of the mercury on the low pressure side cause a stainless steel float carrying a magnetic armature on a non-metallic nickel-chromium rod to move up and down. The stem and float are enclosed in a non-magnetic ferrous alloy tube. Over the outside of this tube a divided inductance coil fits. Auxiliary electrical apparatus passes more or less current, as the divided inductance coil is affected more or less by the magnetic armature within the closed tube. The auxiliary apparatus includes indicating and recording devices.

The metering of fluids by means of a *rotameter* is widely done in the industries. Corrosive as well as non-corrosive liquids and gases are handled successfully; transparent and light-colored liquids present no difficulty; more startling is a development which permits with equal ease the metering of opaque fluids and slurries. This instrument originally depends upon the sighting of the float. Opaque fluids and slurries are handled by means of a float with a rod-extension upward; the top of the rod moves in an upper chamber in which there is no flow. Its position indicates the flow.

The applications away from standard metering which deserve special mention are, for example: the use of a rotameter for measuring accurately the air which is incorporated into the cream for ice-cream before freezing it; the manufacture of sponge rubber, in which rotameters measure a given quantity of air to be incorporated into the latex, instead of merely whipping it up.

The numerous water meters of varying construction are reliable and useful volumetric meters, for all kinds of liquids as well as for water.

FIGURE 276.—The fundamental design of the rotameter for measuring the flow of liquids and gases. The float assumes a position in the tapered tube which corresponds to the volume passed. The direction of flow is shown by the arrows. The rotameter is an orifice meter with variable area. (Courtesy of Fischer and Porter, Hatboro, Pennsylvania.)



ELECTROMETRIC METHODS IN PLANT OPERATION

In a number of industries, the control of the acidity, or in more general terms, of the concentration of hydrogen ions, is of great importance for form production. A number of devices for the electrometric determination of this value have been successfully introduced.¹¹ The development of methods for laboratory use, that is, chiefly analysis,¹² had to precede. This has been in progress for the last fifteen years or so. Two main divisions may be observed.

The first is a conductivity group, in which a measurement depends upon the conductivity of a solution to the electrical current, whether that conductivity be due to acidity, alkalinity, or to salts. If it is known that salts are present, and that only one certain acid can be the cause of the conductivity, a method can be used for the control of acidity.

¹¹ "Progress of electrometric control methods in industry," Henry C. Parker, *Ind. Eng. Chem.*, **19**, 1927.

¹² Consult "The determination of hydrogen ions," Wm. M. Clark, published 1928 by Williams and Sons Co., Baltimore; also the chapter on "Electrometric methods in analytical chemistry," by N. H. Furman, pages 823-863 in Vol. 2 of "Treatise on physical chemistry," H. S. Taylor, New York, D. Van Nostrand Co., 1925.

The second group is the potentiometric group, applied chiefly to the determination of hydrogen-ion concentration in a solution. Its superiority over any other method lies in the fact that it is applicable even in the presence of salts, and to colored solutions which would prevent the use of indicators. The method rests upon the measurement of the potential of a primary¹³ cell made up of two halves, one the hydrogen half, the other the calomel half, a saturated solution of calomel in contact with a potassium chloride solution. Such a cell generates a small current of a definite potential (voltage) if the solution in which the hydrogen electrode rests is normal. The calomel half-cell remains constant. By hydrogen electrode is meant a platinized platinum rod or plate over which bubbles of hydrogen pass at the rate of three a second, or similar rates. If the concentration of the acid solution is varied, the potential of this composite cell will also vary, and the variation will be directly proportional to the change in concentration. Hence this provides a means of following changes in the concentration of the hydrogen ions; with the addition of electrically controlled mechanisms correcting solutions may automatically be introduced. The potential is measured by matching it with a second potential in the opposite direction from an outside source, lowered or raised by the introduction or removal of resistance, until a galvanometer between the two circuits indicates no flow. The amount of the resistance introduced or removed is the real measure of the potential change.

The industrial cell may employ the hydrogen electrode, or this may be replaced by the tungsten or pyrolusite electrode or other non-gas electrodes. A rugged cell entirely protected by a Bakelite sleeve, with all the necessary apparatus transportable, is described in the literature.¹⁴

The electrometric methods of the first class, depending on conductivity, and measured and applied to control by means of a Wheatstone bridge with auxiliary apparatus, serve to detect leakage in surface condensers in power plants. The condensed water is pure and does not conduct the current, but if any cooling water enters through a newly developed hole, let us say it is sea water, the contaminated condensed water will at once allow the current to pass: by means of auxiliary mechanism, a red light will appear announcing the leak.

Control by means of the measurement of the potential due to hydrogen-ion concentration has been applied to the automatic addition of caustic soda and sodium phosphate to boiler feed water which is acid, to maintain the proper acidity in a neutralizing bath for alkali cotton, and to several other industrial problems.¹⁵ Temperature must always be taken into consideration.

A recent development for the rapid determination of carbon in a molten steel while it is in the furnace, open hearth or electric, is the *Carbometer*,^{15a} a Swedish instrument which utilizes the degree of magnetic induction which can be imparted to a test sample of steel; the magnetic induction varies with

¹³ That is, "current-producing cell," in distinction from the electrolytic or "current-consuming cell."

¹⁴ *Ind. Eng. Chem.*, 17, 639 and 737 (1925).

¹⁵ *Ind. Eng. Chem.*, 19, 660 (1927).

^{15a} Carbometer, patent of Malmberg-Holström, manufactured by Aktiebolaget Alpha, Smedbo (near Stockholm), Sweden.

the carbon content. A $\frac{3}{8}$ -inch rod is cast from the spoon sample, quenched, and placed in one of two funnel-shaped vertical receivers in the carbometer; the slot is for hardened steel (over 0.40 per cent C.), the other for unhardened steel. Turning a knob starts the clockwork which drives an armature; the first piece is magnetized. When the armature stops rotating (clicks), pressing a button allows the final rotation of the armature from the highest magnetic field strength position, through 90°, to the lower field strength, inducing a current of electricity in the coil surrounding the test sample. This current is measured on a ballistic galvanometer, shunted in automatically when the armature reaches its final position. The needle reading is translated into carbon percentages by means of a chart, read to within 1 point (0.01 per cent C.). Charts are made at the plant for the types of steel manufactured, inasmuch as other metals alter the magnetic induction. The readings are checked against laboratory analyses.

The refractometer is a useful instrument of control. For example, in the process of hardening vegetable and animal oils to fats, the progress of the hydrogenation may be followed by the change in refractive index. A few drops on the split prism of an Abbé refractometer, with water circulation to give a definite temperature, permit a reading in a few seconds.

An automatic sampling device, for sampling wood chips, or any material from a spout, to a conveyor, for example, has been described.¹⁶

Unit Operations and Unit Processes. In 1915, Dr. Arthur D. Little observed that "any chemical process may be resolved into a co-ordinate series of unit operations, as pulverizing, drying, roasting, crystallizing, filtering, evaporation, electrolyzing, and others." This suggestion has become part of the system of chemical engineering study. A recent addition to the already long list is diffusion.¹⁷ Other unit operations are agitation and mixing, fractional distillation. The process of making caustic soda by causticizing soda ash with lime is divided into four unit operations: lime slaking, causticizing, caustic liquor decantation, lime mud washing. To the unit operations there have been added the chemical engineering unit processes, to the great advantage of the development of the science of chemical engineering.¹⁸

OTHER PATENTS

U. S. Patent 2,020,588, fluid flowmeter; 2,021,615, liquid level indicator; 2,012,616, method and apparatus for introducing reagents into liquid suspensions; 2,022,695, controlling flow of volumes of liquids; on pyrometers and thermocouples, 1,890,701; 1,885,507; 1,820,219, optical; 1,825,229, and 1,788,849, same; 1,845,271, thermocouple; 1,493,332, thermocouple for high temperatures, with a carbon and a tungsten element; 2,370,6, same, but tantalum carbide and graphite elements.

PROBLEMS

1. The outside air is 40° F. and 30 relative humidity. This air is moved into the building, gradually warming to 76° F., with no gain or loss of water. What is the relative humidity for such air in the building, and what would the psychrometer readings be?

Answer: 9 relative humidity; 76° F. dry bulb; 49° F. wet bulb.

2. Starting with any air, how would you furnish a room with air at 72° F. and relative humidity?

¹⁶ *Chem. Met. Eng.*, 37, 350 (1930).

¹⁷ Symposium on diffusion as a basis of Unit Operations, *Ind. Eng. Chem.*, 33, 424 (1941).

¹⁸ "A plea for the Unit processes," by D. B. Keyes, *Chem. Met. Eng.*, 41, 244 (1934).

Answer: Cool or warm to 51.5° F. and saturate with H₂O at that temperature, then warm to 72° F.

3. A sling psychrometer gives readings: wet bulb, 60° F.; dry bulb, 78° F. What is the relative humidity? This air is completely desiccated and then warmed to 78° F. again. What is its relative humidity, and what are the wet and dry bulb readings?

4. For a comparison of heat effects, the following purely theoretical comparison should be made: Air at 80° F. and relative humidity 80, at the rate of 10,000 cu. ft. per minute, passes over a water surface; it takes up more moisture until saturated. How much water in pounds per pound of air are taken up, and how many B.t.u. does their vaporization represent?

To cool this air to 55° F. means the removal of how many B.t.u., equivalent to the vaporization of how many pounds of water? If the heat consumed in the vaporization in the first part of the problem is not sufficient, how many pounds of water at 55° F. will be required to remove the remaining B.t.u. by contact, without vapor exchange?

Take the mean specific heat of the air as is over the range specified as being 0.01826 B.t.u. per cu. ft., and the heat of vaporization for 1 pound of water over the same range as 1060 B.t.u.; take 1 cu. ft. of the air as is to weigh 0.0761 pound.

5. In reality, when 80° F. air with 80 relative humidity is cooled slightly, the temperature will drop to wet bulb temperature, the loss of sensible heat being equal to the gain in latent heat of water vaporized. The latent heat is the heat obtainable when water as gas becomes liquid water. What is the wet bulb temperature which goes with our original datum?

A pound of air at a dry-bulb temperature of 80° F. and a wet-bulb temperature of 75° F. contains 124 grains of water. When such air passes through a spray of water at the same temperature, water will be taken up. The dry-bulb temperature will fall, but the wet-bulb temperature will remain 75° F., and the dry-bulb temperature will equal it. The dew point, which is originally 73° F., will gradually rise to 75° F., when saturation is realized. How many grains of water will it contain now, and what is the gain?

At ordinary temperature, 1 grain of water absorbed means a lowering of about 8.5° F. in the dry-bulb temperature.

6. An air-conditioned system delivers to the space to be conditioned 20,000 cu. ft. of air per minute at 65° F. dry bulb and 40 per cent relative humidity. Of this air, 75 per cent is being recirculated. Determine the refrigeration effect, in tons, required when the outside air has 90° F. dry bulb, and 77° F. wet bulb, the return air has 75° F. wet bulb, and relative humidity of 34 per cent, and the total 20,000 cu. ft. passes through a saturating air washer. Assume 13.6 cu. ft. of air per pound.

NOTE: The standard refrigeration ton is 200 Btu./minute, or 12,000 Btu./hour or 288,000 Btu./day. The value per day is the one generally used. A complete psychrometric chart may be obtained from any firm which manufactures blowers or air conditioning equipment. For example, address the Buffalo Forge Company, Buffalo, N. Y.

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Of the long list of metallurgical products, the production of pig iron and steel exceeds many times that of any other metal. Some of the newer products have received much advertising, necessary because of their newness, but tending to produce a wrong conception of their relative importance. Pig iron and steel are the giants, in war time as well as in peace time, except that in war time they are super-giants.

Chapter 47

Pig Iron*

The manufacture of pig iron is on an enormous scale, as the figures in Table 93 will indicate.

TABLE 93. *World production of pig iron.*

	Gross Tons			
	1929	1932	1935	1939
United States	42,614,000	8,781,453	21,373,699	32,321,653
England	7,580,000	3,573,000	6,426,400	8,300,000
Germany	13,401,000	3,932,026	12,342,415	20,300,000
France	10,439,000	5,537,000	5,799,000	7,900,000
World total	96,263,000	26,578,409	51,070,343	102,464,000

The pig iron production in the United States in 1940 was 46,203,967 net tons; the world production, 120,960,000 net tons. In 1941, efforts were made to raise the production considerably in order to meet the demands for steel in a country sensing approaching war; in 1942, it is expected that the production will surpass all previous figures.

The process in brief consists of heating an iron ore, an oxide, with coke in an upright furnace having continuous operation; hot air under pressure is pumped into the furnace at the base, and by causing the coke to burn, produces a high temperature. The iron oxide is reduced to the metal which collects at the lowest spot, and is tapped off at intervals; the hot fluid iron unavoidably dissolves some carbon (3 per cent). The solids added at the top are iron ore, coke, and limestone; the latter binds much of the silica present as impurity in the ore, and forms with it and other substances the slag, which also flows to the bottom of the furnace. The liquid slag is lighter than the liquid iron and floats on it; it is tapped at frequent intervals through a special tap hole, further up than the iron tap hole. Almost without exception, a mixture of several kinds of ores is preferred to a single one.

The oxide richest in iron is magnetite, Fe_3O_4 , with 72.5 per cent Fe; it is found very pure in Sweden and in a few places along Lake Superior.¹ The next oxide, Fe_2O_3 , nearly as rich in iron (70 per cent Fe when absolutely pure), is the most important one. It is the chief ore of the Minnesota deposits.

Iron ore mined in United States in 1940 amounted to 73,695,899 gross tons, at 230 mines in 19 states; its value was close to 190 million dollars. In Minnesota, 47.7 million tons (64 per cent of the domestic total) were

* Based on studies of a Buffalo furnace, made with the assistance of Dr. Kenneth McVey, Princeton University.

¹ Magnetite deposits occur also in New York, Penna., New Jersey, New Mexico.

duced, in Michigan 12.5, in Alabama 7.3, in Pennsylvania and New York, 0, the rest in smaller states' totals.

As an example of American practice, the Fayal mine in northern Minnesota, about 60 miles from the lake shore (Two Harbors), and part of the Mesabi range deposit, will be briefly described.

The Fayal mine is an open pit mine; the removal of about 20 feet of overburden discloses a vast body of red ore, most of it soft enough to work with a steam shovel. Various levels are worked, as the quality differs slightly; movable railroad tracks are laid on inclines. The empty ore cars are pulled to the desired spot, where a steam shovel (or several) awaits them; the cars are loaded in a short time, without hand labor. A powerful locomotive pulls the cars up the incline and starts toward the lake port, Two Harbors. The train passes at a slow rate over scales, and the weight is read and recorded as the train moves. By the time it reaches Two Harbors, the chemical analysis of the loaded ore is finished and its exact grade determined; this permits a train dispatcher to send the cars to certain pockets in a certain dock, there to be dumped with similar ore. The cars are dumped by pulling the level which opens the bottom. The ore boats are loaded in a simple but rapid way. The ore pockets in the docks are elevated, that by lowering a chute and drawing a gate, the ore is served to the boat by gravity. On approaching, the lake boat whistles its requirements as to quality; a siren at the end of the central dock screeches back signals which tell the boat at which dock, and in front of which pockets in the dock, it should anchor. The boat pulls in with its hatches open, and while still anchored, the chutes are lowered and the ore rumbles into the boat. In thirty-nine minutes it can be on its way out with a load of 11,000 long tons.

TABLE 94.—*Actual reserves of iron ore in the world (1926).**
(Major deposits only)

	In thousands of tons
United States	10,452,225
France	8,164,350
Brazil	7,000,000
Great Britain	5,969,600
India	3,326,110
Cuba	3,159,000
Sweden	2,203,350
U. S. S. R.	2,056,850
Spain	1,115,500
Union of South Africa	1,095,135
Total, World	57,811,923

* "World iron ore reserves now exceed 57 billion tons," O. R. Kuhn, *Eng. Mining J.*, (July 17 1926).

An extensive deposit of hematite containing generally some phosphorus stretches from New York State to Alabama, and is mined in several of the states it traverses.

In order to manufacture pig iron, coke is required as well as ore; in the order of tonnage of pig iron produced, the States are Pennsylvania, Ohio, Indiana, Illinois, Alabama, New York (1940). It will be noticed that the centers of production are those which have coal and coke, rather than ore, and it is a general rule that "ore follows the fuel." The primary production is strict since coke has displaced charcoal and anthracite was Pittsburgh.

where the Connellsville beehive coke was available. The Minnesota ore was transferred to railroad cars at near-by lake ports for the short haul to the Pittsburgh and Youngstown districts. This is still done, but of late years more and more plants have been located at the lake ports, so that the ore boat might unload directly in the yard of the blast furnace plant (Buffalo, Cleveland, Detroit, Gary, Chicago). In Alabama (at Birmingham and other places) the ore and the coal are both found in the district, and in addition the ore contains enough limestone to be self-fluxing. Alabama ore, however, is lower in iron content than Lake Superior ore (35 per cent against 52 per cent). An agency which is at work decentralizing the pig iron industry is the by-product coke oven primarily set up to provide municipalities with gas; it generally has surplus coke suitable for the blast furnace. Along the Atlantic seaboard (Baltimore, Philadelphia) ore from Cuba, even from Sweden, Elba, Spain, and Chile, may be imported at reasonable cost, and with the aid of by-product coke, made into pig iron.²

In England, very pure ores free from phosphorus are mined; with the rich coal resources of Great Britain, the iron industry has long flourished. France has in the Lorraine deposits (now in Occupied France, 1942) a large tonnage of low-grade (30 per cent Fe) ore which contains phosphorus, but also calcium carbonate, so that by skillful working a phosphorus-containing pig iron suitable for the basic Bessemer process for steel, can be made. The deposit is 30 miles long and 12 miles wide, and in its eastern part is mined at the surface. The greater part of the pig iron and steel production of France and Germany comes from this Lorraine ore.³ In Sweden, very pure iron is made with charcoal, from native ores; this pure product is still the basis of the cutlery manufacture of Sheffield. In southern Russia, iron is produced in considerable quantities.⁴ China has rich ore deposits, while her coal resources are second only to those of the United States.

TABLE 95.—*Mesabi Range (Minnesota).*

	Suitable for Acid Bessemer Per Cent	Special Very Low Phosphorus Per Cent	Manganiferous Per Cent	High Phosphorus Called "Non- Bessemer" Per Cent
Iron, Fe	60.72	63.12	53.23	61.37
Phosphorus, P039	.017	.036	.083
Silica, SiO ₂	8.43	7.45	9.37	3.94
Manganese, Mn22	.09	4.77	.38
Alumina, Al ₂ O ₃54	.46	.72	1.60
Lime, CaO25	.05	.31	.15
Magnesia, MgO14	.09	.13	.13
Sulfur, S006	.007	.007	.011
Ignition loss (H ₂ O)	3.91	.95	6.68	5.88
Name of ore	LaRue	Patrick	Silver	Beaver

² Bethlehem, Pa., is not too far from seaboard to use foreign ores, mixed with western Pennsylvania ores.

³ A portion of the deposit lay in the part of Lorraine held by the German empire during 1871 to 1918; its importance was unknown in 1871, for it was only after the English improvement of the Bessemer process, the Thomas-Gilchrist basic lining, that the Lorraine ore could be made into good steel. The effect is plain from the German production figures for steel: 1880, one-half million tons; 1913, 15 million tons. The following figures will indicate the quality of the ore for the Lorraine district, particularly for the Lancy basin, one of the 4 main divisions. Fe 40%, CaO 10%, SiO₂ 6%, Al₂O₃ 1%, P 0.65%.

⁴ 150 miles northeast of Odessa west of the Dnieper, in western Ukraine, lies the Krivoy Rog district, which came into the news in August, 1941, when the Germans claimed its capture. It was said at that time that 61 per cent of the Soviet Union's iron ore output came from this district. In 1938 the production had been 16 million tons of ore.

Several representative analyses ² of iron ores are given in Table 95; much the Minnesota ore is low enough in phosphorus so that the pig iron made from it may be converted into steel in the acid Bessemer converter; other shipments have enough phosphorus to produce a pig which must be melted in the basic open-hearth steel furnace. All analyses are on samples dried at 212° F., hence free from moisture.

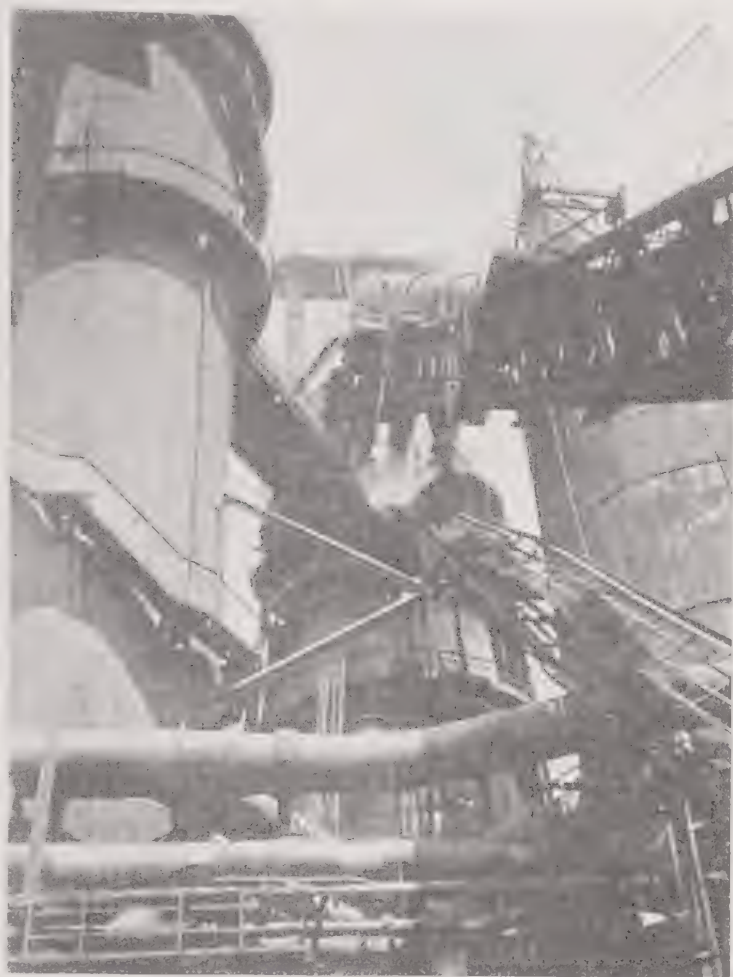


FIGURE 277.—Iron blast furnace and stoves, the Petrovsky plant at Dnepropetrovsk, Ukraine, U. S. S. R. (By permission.)

The ores from other ranges in the Minnesota-Michigan deposits are similar to the four shown in the table, and indicate the same wide variety. The price depends upon the iron and the phosphorus content. If the Lake ore sells for \$4.00, the Beaver may be \$2.00; this is the usual range of market prices. The general average for all ores in 1940 was \$2.51; in 1939, \$2.19.

² Cargo analyses for the season 1925, The M. A. Hanna Co., Buffalo and Cleveland.

THE BLAST FURNACE

The complete blast furnace plant consists of the furnace proper, four stoves, a dust collector, a blowing engine, means of bringing the solids to be charged to the skip hoist, and auxiliary apparatus.

The blast furnace proper consists of a steel shell circular in cross-section, lined with hard fire-brick; the shell stands upright; the upper two-third

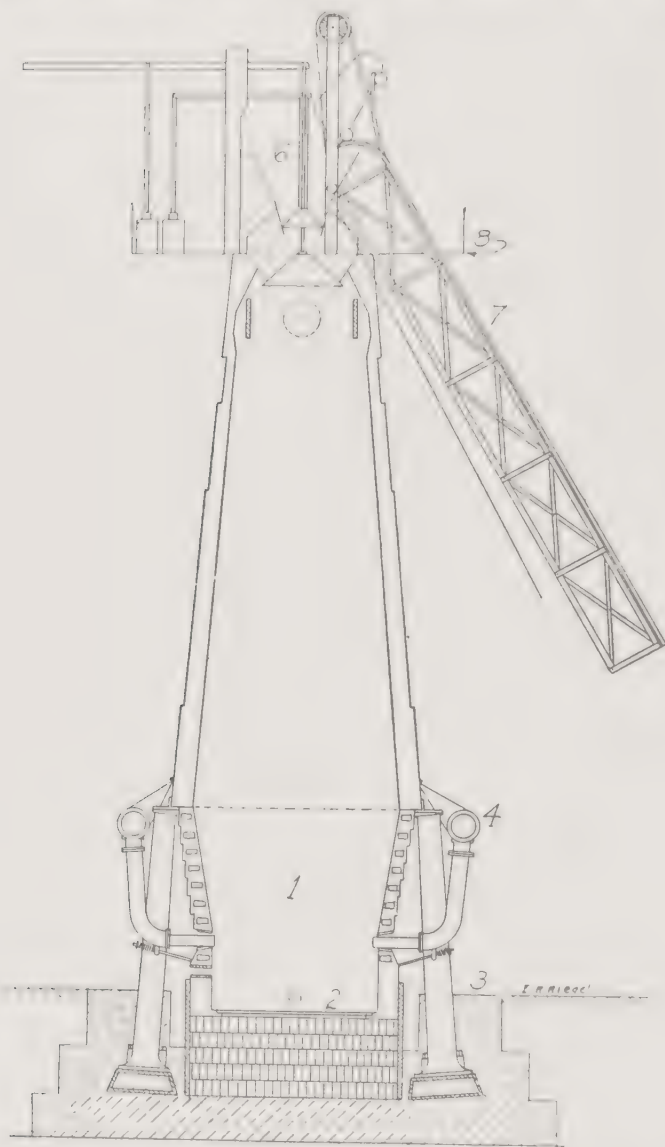
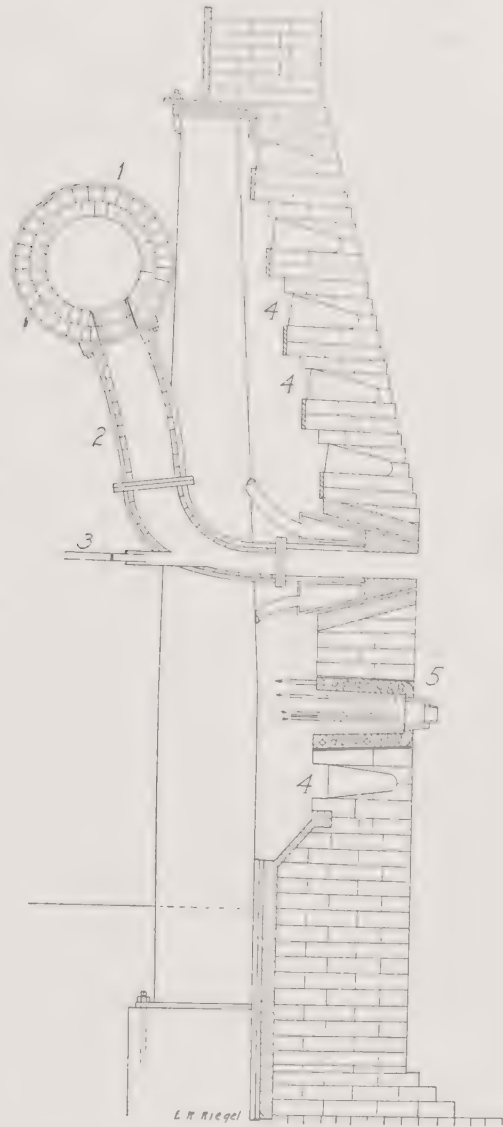


FIGURE 278.—The blast furnace for iron, showing the furnace proper, with 1, the bosh; 2, the hearth; 3, the foundation; 4, the bustle pipe and tuyeres; 6, the double bell for introducing the charge; 7, the skip hoist; 8, platform at top of furnace. The dotted circle under the bell is the outlet for the gases. The distance from 8 to the hearth line at 2 is 92 feet.

or so flare out downward, while the lower third flares in. The purpose of the upper flare is to permit the charge to slide down readily and fill any holes which might develop; with straight sides, it often happened that large cavities formed, so that after a while a sudden descent (or slip) took place, which at times proved disastrous. The lower flare in the opposite sense is required by the removal of the coke by combustion, and

running down of the melted iron, causing a great contraction. The bottom of the furnace is the hearth, where the liquid iron, overlaid by the slag, collects. The charge in the furnace is called the "burden," and is introduced at the top through a vestibule-like arrangement which

FIGURE 279.—Section of the bosh wall in the blast furnace for iron, with 1, bustle pipe; 2, tuyere; 3, sight hole; 4, water-cooled metal boxes; 5, slag hole with water-cooled metal lining.



prevents the escape of gases; the materials fall first onto an upper bell, which is depressed in order to allow the materials to drop into the intermediate chamber whose floor is formed by a second bell. When the second bell is depressed, the charge enters the furnace; at such times, the upper bell is shut tight. This bell is also rotated, so that the charge is placed over the surface of the furnace content. The liquid iron and the

liquid slag are removed periodically by tapping. The slag hole is formed by a water-cooled metal piece, situated above the iron hole; the tapping for iron is in brickwork. At the end of the tapping, the iron hole is closed by a plug of clay, applied by the "mud gun," with a fast-moving piston which forces the clay into the hole. The slag hole is easily closed by an iron plug on a long rod.

The air blast for the combustion of the coke enters through the bustle pipe, a steel pipe 3 feet in diameter lined with fire-bricks, because the air is applied very hot (between 1600° F. and 1000° F.). The blast passes from the bustle pipe to the furnace through the tuyeres, which are partly lined and partly water-cooled. Each tuyere has a sight hole and may be cleared by a rod if anything blocks it from the inside.

The hottest part of the furnace is the bosh (see illustrations) where the tuyeres deliver the blast, and intense combustion of the preheated coke takes place.

The weight of the upper part of the furnace is carried by a number of columns (12 to 18) resting on an elaborate foundation on which the bosh also rests.

The furnace shown in Figure 278 is 92 feet high and 23 feet in diameter at the widest part. In Figure 279, a closer view of the bustle pipe, tuyeres, slag hole, and bosh wall is given; it will be noted that the bosh wall carries metal boxes which are water-cooled, thus lowering the temperature of the brickwork and rendering it more lasting.

The Materials Supplied to the Furnace. Let us consider a blast furnace which produces 1150 tons of pig iron per day. Such a furnace would be a large one, but not the largest. The solid materials fed in per day are as follows: coke 850 tons, limestone 400 tons, ore 2000 tons, divided into 112 charges per day. There are besides occasional additions, such as: every second charge, open-hearth slag, 6000 pounds; every third charge, 5000 pounds of borings; every fifth charge, 1000 pounds of ore containing 5 per cent manganese; and every fifth charge also 1000 pounds of siliceous ore.

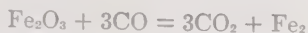
The average consumption of ore per ton of pig iron made in the United States in 1940 was 1.875 tons.

The hot blast which enters the furnace is equivalent to 4040 tons during the day; the rate is 80,000 cubic feet per minute. The pressure is 18 pounds. The air is forced into one stove where its temperature is raised at first to 1400° F., then to 1200° F., finally to 1000° F. as the stove gradually cools. After an hour, the air is turned into another stove which in the meantime has been brought to its highest temperature. Four-fifths of the weight of the blast nitrogen and takes no part in the reaction. It will be noted that the air fed to furnace exceeds the solids in weight.

The stoves are tall steel chambers, lined, and filled with a checker-work of firebricks, in which blast furnace gas is burned with cold air for 3 hours; the bricks gain in heat. Each stove receives heat for 3 hours, and gives up heat over a 1-hour period. If No. 1 is heating the blast, No. 2 is receiving its third hour's heating, No. 3 its second, No. 4 its first. The stoves are of various constructions, but all have an internal downcome; the waste

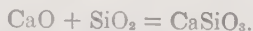
ses may travel through the downcome leading to a chimney, or may be by a stack surmounting the stove.

The Reactions in the Furnace. The main reaction in the blast furnace is the reduction of iron oxide to the metal. Coke burns in the hot blast (the latter is led in by the tuyeres, forming carbon dioxide, and the latter reduced almost at once by the hot carbon adjacent to carbon monoxide. The flames at the mouths of the tuyeres extend over a comparatively limited zone. The carbon monoxide rises and much of it, about a third, acts as the reducing agent:



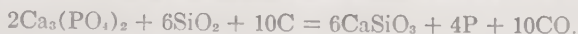
The balance passes to the top of the furnace and passes out in the blast furnace gas, to which it imparts most of its calorific value, unchanged. The simple reaction is an overall result, and a summary of numerous others.⁶ It is very likely that free iron in the spongy form is first formed and melts only later when it passes through the lower part of the bosh; and it is also held that the first reduction is to a lower oxide, which is then later reduced to the metallic iron. The liquid iron contains carbon to the saturation point, in solution, and some in combination.

The limestone loses carbon dioxide, and the lime formed reacts with part of the silica to form calcium silicate:

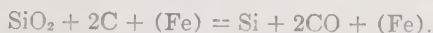


An appreciable amount of iron silicate forms because the lime displaces the iron, thus preventing a loss of metallic product.

The phosphate is present as calcium phosphate, and in presence of calcium, the free phosphorus is liberated and dissolved by the iron:



Silicon is formed from such silica as may reach the hottest region where the combined action of iron and carbon reduce it to the free elements:



Manganese is reduced by carbon at the high temperature of the bosh. Both silicon and manganese are dissolved by the iron. Sulfur, partly if not all from the coke, forms ferrous sulfide which is so heavy that it settles with the iron layer, and not with the lighter slag layer.

The maximum temperature in the furnace, at the tuyere line in the lower portion of the bosh, is generally held to be 2800 to not quite 3000° (1538 to not quite 1649° C.). It then gradually decreases as the gases rise in the shaft of the furnace, until at the top the gas leaving the furnace has a temperature of 400° F. (204° C.). Most of the sensible heat in the gas is transferred to the cold charge, so that the blast furnace is well adapted when it is called a heat interchanger; with the blast furnace gas removed, it might be said also that it is a large-scale gas producer.

Tapping the Furnace. The furnace is tapped for iron five times a day, for example. The iron hole is broken free of the dried clay, and the molten

⁶"Blast Furnace Practice," by Ralph H. Sweetser, p. 159, New York, McGraw-Hill Book Company, 1938.

iron flows out along a gutter lined with firebrick; it passes a small rough-made bridge with retaining box; under the bridge the clear iron flows on over the bridge any slag which was entangled in the metal flows off through a sidewise gutter. The clear metal reaches brick-lined steel ladles capable of holding 70 or 100 tons of metal. Near the end of the tap, the blast is shut off, and when the flow of metal becomes lazy, the clay plug is rammed into the hole. Operation is then resumed.

The slag is tapped every two hours, through its own hole, situated a quarter of a circle away from the iron hole, as well as farther up. The slag is run through a gutter in the floor to a large container on a flat car and pulled to the dump heap, or to a near-by cement plant where it is granulated by cold water and used as one of the raw materials for making a portland cement; there are still other uses for the slag.

The products of the blast furnace thus are pig iron, slag, and blast-furnace gas.

The composition of ordinary pig iron lies within the following limits:

Carbon	3 to 4%
Manganese	0.25 to 2½%
Sulfur	less than 0.065%
Silicon	0.5 to 3%
Phosphorus	0.04 to 2%
Iron	balance, about 92%

There are other "metals" made to suit the orders and purposes.

The Pig Casting Machine. The ladle is carried by the crane to the casting machine and there tilted forward so that the metal is delivered to a box with two side outlets. The box divides the metal into two streams, which feed the buckets of the two endless chain conveyors. A spray of water is played on the slowly traveling buckets, which congeals the iron sufficiently so that at the turn they drop off, still red, as cakes and slide into a waiting car, where they cool to blackness with the aid of more water. Each pig weighs 110 pounds and is 22 inches long, 7 inches broad at the base, and 4 inches thick.

In many blast-furnace plants, there is no need of casting the metal into pigs, for it is to be used at once for steel making in the open hearth, or in the Bessemer converter. For such purposes the iron is never taken directly from the blast furnace to the steel furnace or converter, but it is delivered first to a very large ladle capable of holding several taps; this large receiver is called the mixer. It offers the great advantage of furnishing a very uniform metal, avoiding single taps with just enough irregularity of composition to prevent the metal from giving the usual results. In some installations, the mixer is more elaborate still and the opportunity is taken to burn off some of the sulfur by playing a stream of burning gas over the surface.

The Blast Furnace Gas. The gas which passes out at the top of the furnace has been cooled considerably by the cold portion of the burden, which gains the heat which the gas loses. The gas is cold enough to be passed through a steel flue to a steel dust-catcher, and from there to a gas washer, a box through which a fine spray of water descends, while the gas

nds. The cleaned gas is made to work in several ways: to raise steam for the driving of the blowing engines, as internal gas fuel for the gas engines driving the air compressor, if such are used, and to heat the stoves but by means of the latter the incoming blast may be heated. The gas is not rich in combustibles, but it contains enough to furnish the heat required for the purposes stated above; usually there is surplus gas, which in some cases is piped to households of employees. The heat value of the gas is due to its carbon monoxide content:

	Per cent
Hydrogen, H_2	1.0
Nitrogen, N_2	59.6
Carbon monoxide, CO	26.0
Carbon dioxide, CO_2	13.4
B.t.u. of the blast-furnace gas	87

Pig iron prices are different for the seven varieties marketed, which vary exceedingly in tonnage. The leader is basic pig iron, the average price for which was \$17.33; the next is Bessemer pig, which brought \$19.67 a ton. The average price for all grades was \$17.90.*

A reported improvement was the removal of water vapor from the air entering the blast by refrigeration (Gayley). Water vapor reduces the temperature at the bosh; since it varies from season to season, it makes the operation of the furnace irregular. The capacity of the furnace is increased, and the coke consumption slightly decreased. There are still many furnaces, however, which do not dry the air, and yet show excellent results.

A proposal has been made to enrich the air with oxygen from liquefied

The making of iron castings is described in Chapter 45.

SPONGY IRON

Large-scale experiments in rotary gas-fired kilns in order to produce sponge iron directly from the ore without first making pig iron have been successful. Ore and coke enter at the upper end; after drying, the reduction takes place in about 1 hour; the reduced product is discharged at the lower end. After cooling, the iron is separated from excess carbon and from ash by a magnetic separator. There is no fusion of the iron in the kiln, hence the fuel consumption is much lower. The permissible range of temperature is between 875° and 1025° C., with 950° C. the most desirable

WROUGHT IRON

The earliest form of iron, obtained from the oxide ore by heating it with charcoal to the softening point, and then laboriously worked over ("puddling") at the heating place by handtools, with the metal never free from slag, lost its importance with the installation of the processes which produce Bessemer steel and liquid cast iron. Nevertheless, wrought iron is still being made, mainly because it has high corrosion resistance. Hand puddling was

Other types of commercial combustible gases will be found in Chapter 15. Other analyses of blast-furnace gas will be found in *Chem. Met. Eng.*, 10, 713 (1912).

Iron and Steel Yearbook, 1940.

Compare Chapter 19.

Iron Steel Inst., 111, 491 (1925).

succeeded by mechanical puddling, itself supplemented by lagoting; the most modern and striking method, with rapid and high output, is the Aston¹⁰ process, also known as the Byers process.

Wrought iron is defined as a ferrous material, aggregated from a solidifying mass of pasty particles of highly refined metallic iron with which, without subsequent fusion, is incorporated a minutely and uniformly distributed quantity of slag. It is the presence of the slag which gives it a fibrous structure.¹¹

In the Aston process, the pig iron is melted in cupolas and blown in Bessemer converters according to the usual practice for steel (see next chapter). The blown metal is tapped into a ladle, then poured into molten slag contained in the processing ladle. The slag is held at a temperature several hundred degrees lower than the freezing point of the refined metal; the latter is continuously and rapidly solidified. Such rapid solidification causes the dissolved gases to burst out with sufficient force to shatter the metal into small fragments which settle to the bottom of the ladle, when they weld together, aided by slag particles, into a sponge. At once the excess slag is poured off, and the sponge ball (6000 to 8000 lbs.) dumped at the rate of one every five minutes on a platform of a 900-ton press, where it is squeezed into blooms ready for rolling.¹¹

Wrought iron has low carbon and low manganese content. For example, Byers No. 1 contains C 0.08 per cent, Mn 0.015 per cent, Si 0.158 per cent, P 0.062 per cent, S 0.010 per cent, slag by weight 1.20 per cent.

The production of wrought iron pipe and tubing, the most important outlet, was 35,879 tons, in 1935; the corresponding articles made from steel totaled 928,526 tons for the same year. Plates, sheets, bars, and other products are also made of wrought iron, to a limited extent.

Electrolytic Iron. An extremely pure iron is deposited by electrolysis from a solution of ferrous chloride. In the Boucher-Bouchayer process, developed at Grenoble, France, the metal coats rotating mandrels until the desired thickness is reached. The tube so formed is stripped off; it is very brittle because of dissolved hydrogen. The brittle metal may be powdered and fashioned into a coil with the aid of a binder; such a coil has low hysteresis losses and is valuable as an electrical device (example: the Pupin coil). By heating the tube in a furnace, the hydrogen is driven off and the brittleness disappears. During the electrolysis, ferric chloride is formed; this is the solution used for preparing the electrolytic bath by allowing it to act on iron sulfide, FeS , obtained by burning pyrite or pyrrhotite, Fe_7S_8 . A plant established in America has been discontinued.

OTHER PATENTS

U. S. Patent 2,057,919, influencing the chemical and physical properties of blast furnace slags; 1,984,793, production of pig iron and Portland cement in a blast furnace; 1,941,983, reducing iron ore; 1,964,402, same topic; 1,963,269, desulfurizing and purifying iron; 1,837,696, electro-thermic reduction of iron ores; Ore, carbon, and slag are introduced into a horizontal hollow graphite electrode; the charge is pushed gradually down the passage, gaining in heat, until the hottest zone at the mouth of

¹⁰ The patents granted to James Aston, on the manufacture of wrought iron, are: U. S. Patents 1,255,499; 1,413,513; 1,820,177; 1,890,637; 1,987,598; assigned to the A. M. Byers Company, Pittsburgh, Pa.

¹¹ See chapter on "Wrought iron," by A. W. F. Green, "Metals Handbook," 1936, Chemical Co. pp. 337-343.

material is melted when reduction takes place. The melted non (cast non position) collects in a fore-chamber, which is tapped at intervals.

PROBLEMS

1. In the present chapter, is there an example of the countercurrent principle worth mentioning?
2. Let the ore charged in the specific example for the blast furnace given in the text contain 50 per cent Fe, and assume that the dust loss is nil, also that there is no gas loss; compute the weight of iron which will be obtained, assuming the pig iron to be 92 per cent Fe.
3. Set up figures to show how many tons of the several materials are required to produce one ton of pig iron, from information given in the text.

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- The iron furnace," T. L. Joseph, *U. S. Bur. Mines T. C.* 6779 (May, 1934). See *R. I.* 3229, and *R. I.* 3240.
- Blast furnace practice," Ralph H. Sweetser, New York, McGraw-Hill Book Co.
- The making, shaping and treating of steel," J. M. Camp and C. B. Francis, 5th ed., Pittsburgh, Pa., Carnegie-Illinois Steel Corporation, 1940. *Pig iron*, p. 223-297.

The production of steel in 1940, for the United States, was 67 million short tons. In 1942, it is expected that the production will not be far from the rated capacity, 91.1 million tons per year. The making of steel on this huge scale is an industry only about 72 years old; it dates from the invention in 1855 by Henry Bessemer, an Englishman, of a new method of purifying pig iron, the usefulness of which was extended (1878) by Thomas and Gilchrist, also Englishmen. The process of Bessemer was discovered independently by William Kelly, of Kentucky, in 1847.* The other main process for steel is due to William Siemens, an Englishman, and to E. and F. Martin of France (1865). Several of the important improvements of a later date are due to Americans.

Chapter 48

Steel

Steel is a purer iron than cast iron; the undesirable impurities of the latter, silicon, phosphorus, sulfur, and manganese, are either removed or reduced to a very low amount except on special orders; carbon, which is 2.5 to 4 per cent in cast iron, is reduced to 0.2 per cent for a very soft steel, 0.55 for rail steel, and perhaps 1 per cent for extra-hard steel, in all cases distinctly lower than in cast iron. It will be noted that the amount of carbon in the steel, varying between the comparatively narrow limits of 0.20 to 1 per cent, regulates the hardness of the steel. The manufacture of steel is then essentially a purification of pig iron, by slagging the phosphorus, silicon, and manganese, and removing the excess carbon by oxidation; the raw material is not pig iron alone, but to a large extent steel scrap of all kinds. The proportions of pig iron and scrap are not fixed but depend upon market conditions. The removal of the impurities effects a profound change in the properties of the material; the brittle, comparatively weak cast-iron, which cannot be rolled, is transformed into the strong, tough steel, which may be rolled and forged while at red heat. The melting point rises. Table 96 shows the difference in some of the properties:

TABLE 96.—*Properties of iron and steel.*

	Specific Gravity	Tensile Strength Pounds per sq. inch	Melting Point		Carbon Content Per Cent	May Be Rolled
			° F.	° C.		
Pig iron (gray)	7.3	15,000	2000	1093	2.50-4.00	No
Medium steel	7.8	65,000	2500	1371	0.15-0.30	Yes
Rail steel	7.8	110,000	2500	1371	0.55	Yes

Steel has the further advantage of acquiring a "temper," varied according to the details of treatment, by heating and quenching; heating and slow cooling removes the temper.

* U. S. Patents to William Kelly, 16,444 (1857), combination of the hearth of a blast furnace with auxiliary tuyeres bringing a blast of air; 17,628, blowing blast of air, hot or cold, through a mass of liquid iron, the oxygen combining with the iron, causing a greatly increased heat and boiling commencing in the fluid mass and decarbonizing and refining the iron; 18,910, claim 1, conducting a blast of air through the liquid iron to near the bottom of the hearth; claim 2, refining and decarbonizing simultaneously in the hearth of a blast furnace and in an adjoining chamber having communication therewith.

The steel produced on a large scale has become a structural material of great importance, replacing stones and bricks, and making possible the building of bridges which otherwise would not exist. The American skyscraper would have been impossible without steel. The extension of railways is due also to the large-scale production of steel, not only for the rails, but also for the locomotives. Stationary high-pressure boilers, steam engines and turbines, machines of all kinds depend upon the production of steel. The two processes by which such steel is produced are the Bessemer converter process and the open hearth process; the two produce essentially the same kind of steel.

There are in addition a large number of special steels, with properties fitting specific purposes, many of them of great importance, although the amount used may be small. Examples are: self-hardening tool-steel, nickel steel for armor-plating, chrome steel for navy guns; these will be described briefly further on, and also the process of combining a hard surface with a tough, strong interior, by case-hardening.

OPEN HEARTH PROCESS

The open hearth process was introduced some 10 years after the Bessemer converter. The charge is placed on the hearth of a large brick furnace heated by gas or oil fire, and the heating continued, with occasional

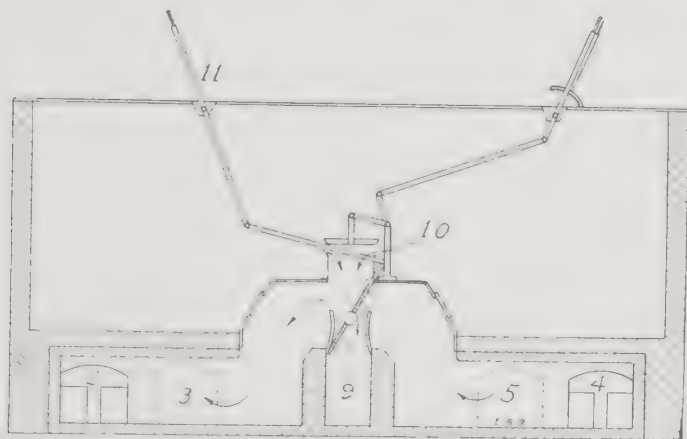


FIGURE 280.—Air reversing mechanism; 10, entering cold air; 3, regenerator for preheating the air; 5, fire gases leaving the second regenerator for air, and passing to the stack at 9; the butterfly valve is reversed at 11. A valve for controlling the amount of air is also provided.

tions of fluxing materials, until the carbon is sufficiently low; the product is tapped at intervals.

As example of open hearth furnace practice, a specific furnace with a hearth 19 feet broad by 34 feet in length, with a capacity of 100 tons every 4 hours, will be described. The hearth is on a level with a working floor sufficiently elevated so that on tapping, the metal may be run into a ladle, the ladle, standing on the ground floor; this provides at the same

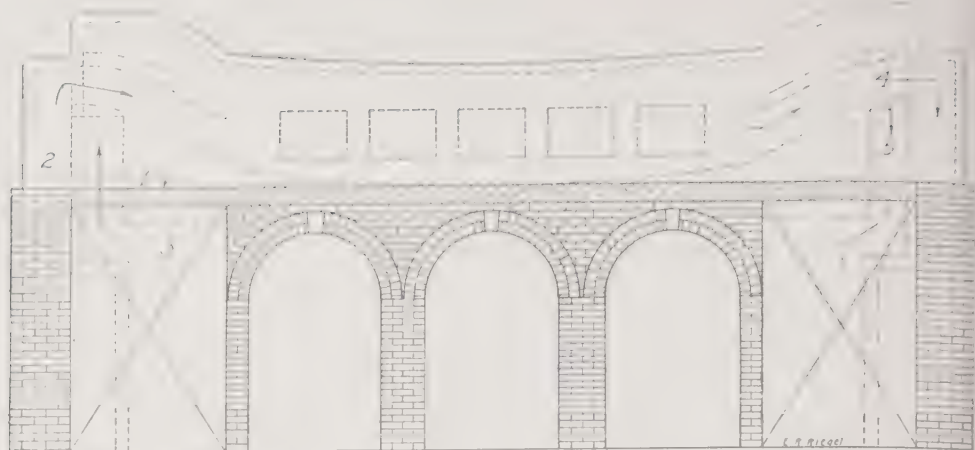


FIGURE 281.—Front view (elevation) of the open hearth furnace for steel. 1, working floor; 2, entering hot producer gas; 3, entering hot air blast; 4, fire gases passing to regenerator for gas, and 5, for air. The same numbers for blast and air are used in the several sketches.

time space under the furnace for the brickwork of the regenerators. The fuel is producer gas,¹ preheated in a regenerator; the air is also preheated. Air and gas enter by separate ducts at the left of the furnace, mix, and sweep while burning over the hearth, and pass out at the right, reaching two regenerators which they heat, before escaping to the stack. There are in all 4 regenerators to each furnace; the direction of the gas and air is reversed every

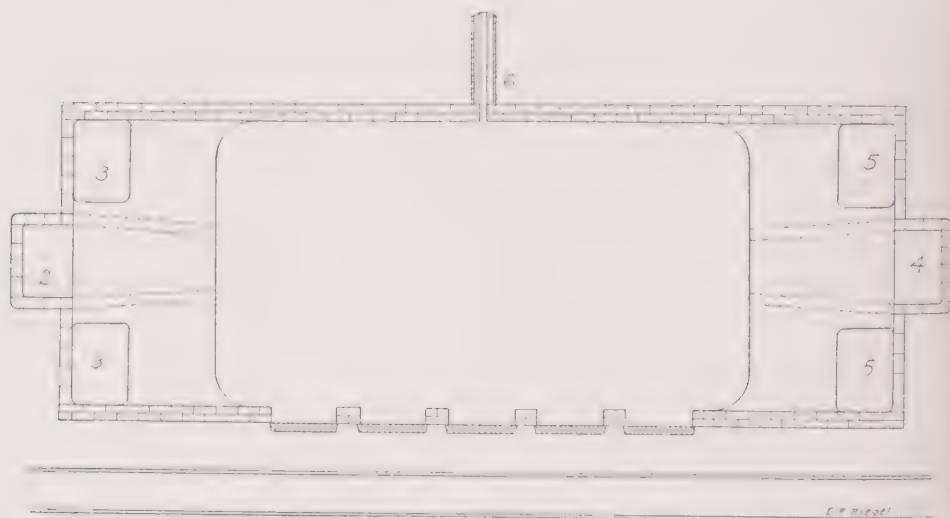


FIGURE 282.—Floor plan of the open hearth furnace; 2, gas entry; 3, air entry; 4, fire gases to gas generator; 5, fire gases passage to air regenerator; 6, tapping trough, at the rear of the furnace.

15 minutes, by hand operation of levers which control the compressed-air mechanism which swings the valves. A scheme for the reversal of the air is shown in Figure 280; a second similar arrangement reverses the gas flow

¹ Chapter 15.

Several views of the furnace (Figs. 281-283) will add to the description. The roof of the furnace is rather high (8 feet) in order to give room for the charging pans. The doors are water-cooled steel doors, operated by compressed-air mechanism with distant control.

The furnace has 5 working doors which face the working platform; all the work is done on this side except the tapping, which is done at the rear (compare Fig. 283). The furnace floor is built of clay bricks, covered with magnesite bricks,² and these are covered with magnesite lumps of assorted

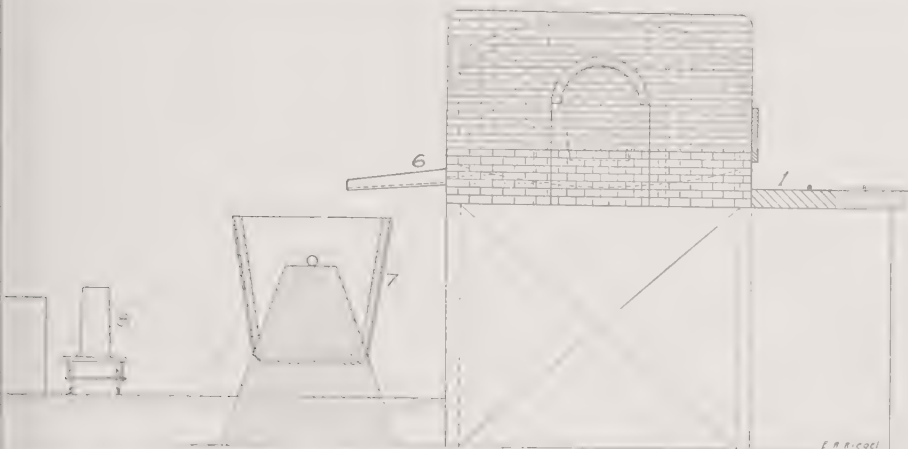


FIGURE 283.—Side view (elevation) of the open hearth furnace, showing the relative location of working floor 1; tapping trough 6; ladle 7, and ingot mold 8.

are mixed with 15 per cent basic slag, well burned in. The roof is lined with fire-bricks. On the floor, calcined dolomite is thrown by hand shovels before every charge, and the furnace is then ready for the run or "heat." The charge consists of

- 125,000 pounds of scrap iron, mainly ends of sheet steel
- 25,000 pounds of cold pig iron, from the storage pile
- 100,000 pounds of melted pig iron just from the mixer
- 26,000 pounds of limestone
- 500 pounds of fluorspar added at intervals during the 11 hours
- 2,000 pounds of iron ore, such as hematite

The cold materials are in narrow pans, 4 to a truck (rails). A steel casting machine moves on rails along the platform, and lifts each pan, pushes it into the furnace through the opened door, rotates it to dump the contents, and pulls it out again, by means of a mechanical arm with inside movable jaws; the pan casting has the necessary slots to receive the arm lock. The cold pig is poured from a ladle hung from an overhead crane into a trough through one of the working doors. After all the materials have been added and are melted, the depth of the liquid metal on the hearth is about 24 inches. With the charge in the furnace, there is little to do except to reverse the flow and observe the progress of the reaction, until near the end of the period.

90 to 93 per cent MgO .

The relative amounts of pig and scrap vary. It may be 40 per cent pig as liquid iron, tapped for example from the mixer at the foot of the blast furnace, which holds 3 or 4 blast furnace taps, and 59 per cent scrap, with perhaps 1 per cent ore added merely in order to reduce the great amount of carbon which the pig iron brings. Or, it may be the "pig and ore process," with 70 per cent pig, 30 per cent scrap, and 12 per cent iron ore based on the metal and scrap. In this latter case, a sizable portion of the final steel come from the ore directly.

It will be well to remember that in any case a vast amount of carbon is brought to the furnace, and the essential function of the open hearth becomes the removal of any excess carbon by combustion, along with removal of phosphorus, sulfur, and silicon.

Progress of the Heat. The operator observes the appearance of the mass at the peep hole in each door, through blue glasses. The temperature is 2400° F. (1315° C.) at first, and increases to 2800° F. (1538° C.) and even 3000° F. (1649° C.); after a time, the charge is melted and the liquid appears to boil violently. A part of the boiling effect is due to the escape of gases occluded in the metal, a part to carbon dioxide escaping from the limestone, and another part to the carbon monoxide from the carbon in the pig iron, burning with the oxygen of the hematite and of the furnace gases. There are two ways for the rapid determination of the amount of carbon still present in the metal. The older way is to take a spoonful of metal and pour it into a mold to form a small pig which is quenched and then broken in two. From the appearance of the fracture, the trained eye of the operator can tell the carbon content with remarkable accuracy. The latest method is the carbometer,^{2a} an instrument which measures the magnetic induction in a rod of steel cast from the metal in the furnace. With a few motions and in less than a minute, the "melter" knows the carbon content within one point (0.01 per cent C.). Besides these rapid tests, it is not infrequent to hold the furnace quiet while an analysis is made in the nearby laboratory. After 11 hours, the carbon content has been reduced to the desired point and the furnace is ready to be tapped.

Over the liquid metal there collects gradually a layer of slag, containing the impurities. Oxidized silicon and phosphorus form, with the lime from the limestone, calcium silicates and phosphates, which are melted and float on the metal, because their specific gravity is lower. The fluorspar is added to make this slag layer thinner, more readily separated from the steel.

The changes in the basic open hearth furnace are indicated in the figures below.

Changes in basic open hearth furnace.

	Charge	Steel
	Per Cent	
Carbon	1.0	0.18
Silicon	1.40	.004
Phosphorus	0.05 to 2.5	.02
Manganese	1.80	.44
Sulfur1	.042
Iron	93.2	99.3

^{2a} The carbometer is described briefly in Chapter 46. A set of curves giving carbometer readings against per cent carbon appears on p. 162, *Metals Progress*, 31 (1937).

An additional example of open hearth practice is given under "Outline processing of heat," to show especially the rate and method of removal carbon, as well as other particulars.

Outline of processing of heat.

Basic open hearth steel furnace in an American plant, 1941.

Analysis: Tolerances in specifications, C .63 to .67; Mn .70 to 1.00; P not over .04; S not over .040; Si .20 to .30.

Finished steel produced tested as follows:

C .65; Mn .92; P .017; S .020; Si .27.

Open hearth: Started charging 4:50 a.m.; finished charging 6:10 a.m.

Total time of heat 9 hours 27 minutes.

Charge: Limestone 24,000 pounds; home scrap 118,000 pounds; hot metal (pig iron from the mixer) 119,000 pounds.

At finished lime" (when lime comes to the top) C was 1.19; ore added 2500 pounds bon dropped as follows, and additions made as shown:

11:08 a.m.	—1.19	
11:45	—1.08	
11:50	—	2000 lbs. ore
12:20 p.m.	— .87	
12:32	— .85	
12:35	—	600 lbs. fluorspar, to thin the slag
12:40	—	500 lbs. ore
12:55	— .72	
1:00	— .71	
1:06	— .69	
1:12	— .68	
1:18	— .67	
1:24	— .66	
1:29	— .65	
1:35	— .62	
1:37	—	1200 lbs. spiegel iron for a wash
1:44	— .61	
1:49	— .58	
1:50	—	1200 lbs. spiegel
1:56	— .59	
2:01	—	1200 lbs. silicon pig (15% Si)
2:06	— .59	slag tested at this time, must not be too high in FeO; it tested FeO 8.49%; Fe ₂ O ₃ 6.29%
2:07	—	2100 lbs. ferromanganese (Mn 80%)
2:17	—	start of tap
2:24	—	finish tap; T of steel as it run into ladle 2900° F.

Final additions: 0.276% Si (1200 lbs. 50% FeSi); enough aluminum to 118 tons of steel, to make 1.18 lb. per ton (bar Al).

Interval between start of tap to start of pour: 9 minutes.

Turning ingots, into molds with hot top:

Size of nozzle 1½ inch; pouring temperature, 2nd mold 2828° F., 20th mold 2828° F.

Sampling pit record: Surface temperature when drawn from the pit 2185° F.

Rolling and billet mills: Av. temp. of blooms leaving 44" mill 1888° F.; av. temp. of billets leaving 32" mill 1903° F.

Note: The ore is added to lower the carbon by oxidation; ore contains about 50% Fe. Carbon test by Carbometer; manganese removes sulfur.

Tapping the Furnace. A ladle with the capacity of 100 tons (15 feet high) of brick-lined steel, with nozzle in the bottom, has in the meanwhile been placed in position at the rear of the furnace. The taphole is cleared with a bar and a stream of oxygen; if the hole does not form, a small pig, which is hot, is brought from the front of the furnace and placed in the taphole; a stream of oxygen is played on it and the high temperature so produced melts the cold steel and opens the hole. The steel at white heat flows

out through a short trough into the casting ladle; slag runs out near the end and is run off from a side trough at the top of the ladle and forming part of it. The ladle is lifted by an overhead crane traveling in the rear of the furnaces, and carried over the ingot molds.

Casting Steel Ingots. The ingot molds are made of cast iron, open at top and bottom; they are set each on a heavy steel or copper base plate, carried on narrow trucks on rails, 6 to a truck. The bottom of the mold is formed by the heavy base plate; a little sand at the edges prevents the metal from running out. The ladle is brought over the mold, and the fire-clay plug lifted from the fire-clay nozzle in the base by a rod (with protecting fire-clay sleeve) operated from a second rod running down the side of the ladle. After one mold is filled, the plug is lowered into place, and the ladle is moved to the next. Each ingot weighs about $2\frac{1}{2}$ tons, is 19 inches square (with rounded edges) and about 5 feet high.

An improvement in the casting procedure consists in placing over the top of the mold a stoneware sleeve as wide as the mold itself, and allowing the metal to rise within it. This "chimney top" does not chill the metal, allows the gases to escape, and prevents, by feeding hot molten metal downward, the large cavity formerly formed in the upper part of the ingot. A further advance is "scarfing," namely, cutting away with an acetylene torch the bad metal from the corners of the ingot.

Rimming Heat. There are to be distinguished the "rimming heat," the "killed heat," and an intermediate one, "semi-killed heat." The rimming heat may be illustrated by a manganese rimmer, a steel to be used for nuts and bolts stock. Such a steel must contain sulfur, which may be as high as 1 per cent; in this case it will be more moderate. During the progress of the melt of 100 tons, there will have been added 1000 lbs. of manganese; and while the tapping is in progress, there are added to the ladle, which takes the whole of the "heat," that is, of the tap, 300 lbs. of brimstone, 60 lbs. of anthracite to restore carbon and bring it to the required percentage, and finally 1400 lbs. of manganese in the form of 80 per cent (ferro-) manganese. The resulting steel contains, in this case, 0.16 to 0.18 per cent C, 0.55 to 0.65 per cent Mn, 0.10 to 0.12 per cent S. As the steel is poured from the ladle into the ingot molds, the liquid steel "works," that is, bubbles, for several minutes. On cooling, the ingot will be found to have a crust of close-grained metal along the outer walls, with a core of coarser grained metal, darker in color; hence the appellation "rimmed." The ingot passes through the blooming mills, and is reduced in size in other mills, undergoing continually an elongation, but never losing this composite structure of fine grained rim with coarser grain core. The purpose of the sulfur addition, and other additions in definite proportions, is to produce a steel which will give short turnings when threaded, which then fall off easily and do not plug the dies in the automatic screw-making machines. The sulfur is present in the form of manganese sulfide. The steel just described is for "hot heading" such nut and bolt stock; a somewhat different composition is selected for the "cold heading" stock, with the carbon .15 per cent and the manganese somewhat higher.

Killed Heat. A high manganese steel will illustrate the "killed steel"; such a steel might be spoken of also as a high-impact steel. The bath in the open hearth furnace is brought along in the usual way, with the addition of a certain amount of ferro-silico-manganese (66 per cent Mn, 18 per cent Si). Near the end of the period, there is added a "wash" of pig iron; these sink in the melt, and cause a violent action from below which drives upward any sluggish impurity which is to be slagged. Next a "block," some 3000 lbs. of silicon-manganese iron are fed in. This addition melts and quiets the bath, giving an interval with essentially no "work," hence no change in composition; that period is utilized to make a laboratory analysis for carbon and manganese. It should be said that the quietness of this interval is helped by shutting off the gas and air. Guided by the analysis, the proper amount of 80 per cent manganese is placed in the furnace, and it is ready for tapping. To the ladle, as it fills, there may be added anthracite. The final composition is 0.30 per cent C., 0.55 to 1.75 per cent Mn, not over 0.03 per cent P, not over 0.04 per cent S. As the ladle is lifted over the ingot molds and fills these, the steel does not "work" at all; it is quiet, and begins to solidify at once; all action in the ingot mold has been "killed." The metal is essentially uniform over cross-section. This steel fits S.A.E. T1330.

For this high manganese "killed" steel, the hot top chimneys are used over the ingot molds.

Semi-killed steel lies between the rimmed and killed steels.

Soaking Pits. The small trucks with the filled molds are pushed under a shed in which an overhead crane travels, which carries special lifting claws fitting the mold. The claws engage the mold and lift it up, leaving the ingot (still red) standing on the platform; the mold is placed in an empty truck ready to return to the furnace building. Any mold which fails to leave its ingot is reworked in the furnace, mold and ingot. The stripped ingots are conveyed to the mill building, and first reheated to bright red heat in the "soaking pits." The pits are brick-lined chambers the floor, 6 feet deep and 4 by 6 feet in cross-section, heated by gas. As a rule, four pits are served by one gas main.³ The transfer of the ingots to the pits and their removal is done again by an overhead crane, carrying a grabbing tool (the dog). The reheated ingot is deposited in a steel basket on an electric truck, which carries it to the first of four or five mills, where it simply dumps the basket, so that the ingot lies on its side ready to enter between the two rolls of the mill.

Rolling Mills. The ingot enters the first set of rolls of the mill (sometimes called the blooming mill) which reduces its thickness; it is returned to the rolls after being turned on its other side by mechanical claws, so that all four faces are pressed; it is at the same time elongated. This treatment is repeated in the next set of rolls, the steel billet lengthening on each passage while its diameter diminishes. In order to make steel rails, the rolls have grooves arranged so that two which revolve on each other give a passage approaching the shape of the rail cross-section; the last

³A sketch of the soaking pit will be found on p. 219, "The metallurgy of iron and steel," by Percy Stoughton, New York, McGraw-Hill Book Co., 1913.

passage has exactly the shape of the rail. The imperfect ends are cut off by heavy shears and returned to the open-hearth furnace. Each mill has two (or three) horizontal rolls, with several grooves for the smaller rolls, of gradually diminishing size; the steel may be passed back through the same rolls, forward again and back again, a number of times, each time through a smaller passage; the method of moving the steel is by smooth rollers forming the floor on which the piece rests; the floor rollers may be revolved at any speed, and may be reversed at the will of the operator, who stands at a distance on the control platform. The floor rollers as well as the mills are driven by steam engines or D. C. motors, through gears with V-shaped teeth. To keep the mill rolls from heating, a small stream of water is allowed to flow over them; some of it reaches the steel, but has no appreciable effect.

As the steel rail emerges from the last passage, it travels to a revolving saw which cuts its end true; it then moves on to a stop which controls its length; the saw makes another cut. A second length is measured off and cut, and the waste end sent back to the furnace. The rail, which is still red hot, is moved to a storage shed (floor rollers), where floor claws push it along resting bars toward one end of the room, to cool. One ingot of the size given makes two rail lengths, and the time required from the blooming mill to the shed is about 15 minutes.

Not only rails, but flat iron, bars, angle irons, tees, channels, and I-beams are shaped in this way. Wide flat iron (skelp) is bent and welded to form tubes (iron pipes of all sizes) by automatic operations.⁴

The process of rolling is not merely a shaping of the mass, but because of the pressure applied in the mill, the particles in the steel are pressed together, coarse particles destroyed, and the strength of the material increased.

A distinction is made between the basic open hearth and the *acid open-hearth process*; in the basic open hearth, which is the more important one, pig iron and scrap containing 2 per cent of phosphorus and even more may be used, for by the addition of lime, this phosphorus, after oxidation to its oxide, is fluxed out as calcium phosphate. The acid open hearth, the original process, makes no provision for the removal of the phosphorus: pig iron or scrap with a low phosphorus content must be used (0.045 per cent P), and the steel will contain a slightly higher percentage. The acid open hearth is used in England. Four-fifths of the rails produced in the United States are open-hearth steel.

Continuous Strip Mill. Increased demand for sheet steel has made a more rapid and more economical method of production desirable, and this has been realized in the Mesta machines, which roll a slab into a continuous sheet of steel at a rate not unlike the rate of paper-making on the Fourdrinier.

A slab, let us say for illustration, 35 inches wide, 13 feet long, $4\frac{1}{2}$ inches thick, of low carbon steel, preheated to 2300° F. (1260° C.), is pushed (mechanically) onto rollers forming the first part of a long roller platform

⁴ The National Tube Co., McKeesport, Pa.

interrupted only by the rolling mills. From here on, the steel travels in a straight line, in one direction. The slab is fed successively to each of the stands called "four highs," each operated as single units and at individual speeds. Each "four high" rolling mill consists of 4 rolls, arranged vertically; reading from the bottom up, they are: an idler, a driven roll in contact with the slab, the gap through which the steel passes, an upper driven roll, and finally another idler, the "back-up." A scale breaker strikes the slab as it moves from the first to the second of these preliminary stands. Beyond the fourth stand, the slab reached a space called the "cooling table," where it can be moved back and forth until it has cooled to the proper temperature for the final pass, namely 1620°F. (882.2°C.). The slab is, by now, considerably elongated, and much thinner, perhaps $\frac{3}{4}$ inch. It now enters the first of a set of 6 stands, also "four highs," passing directly from one to the next and emerging from the last, with the prescribed thickness or gauge. These 6 "four highs" reduce the thickness of the steel stepwise; they have different speeds of rotation^{4a} taking up exactly by the increment of speed the increment in length. The width is set by side guides. The mill red sheet hurries down the long table (with driven rollers for floor), and wind itself automatically into a coil, which is pushed out and dumped onto a floor conveyor traveling at right angle to the long table.

The maximum speed on leaving the last of the 6 "four highs" is 1350 feet per minute, for the lowest thickness (.050"); the minimum speed for the heavier gauges is 200 feet. For the medium thicknesses it is around 600 feet; this means that the observer, standing on the bridge over the hot mill table, will see the red sheet rush by below him in 30 seconds, for a length of 180 feet,^{4b} a frequent length. The time from slab to coil is 2 minutes.

The clearance at the last mill is still much greater than the thickness of the steel; for example, a clearance of .220 inches is used to produce a sheet .074 inches in thickness.

The hot mill capacity is 50,000 tons a month. The width of the sheet may be as high as 72 inches.

After cooling, the coil is passed unwound through the pickler (dilute HCl), is washed, dried, and oiled, and next *cold rolled*, with a reduction in thickness of 60 per cent. This considerable reduction is accompanied by the creation of strains, and brittleness, so that the cold rolled sheet, now cut to convenient lengths (a popular size is 68 inches by 120 inches), is made up into piles and covered with an annealing oven. The atmosphere of the oven is controlled; the box is filled with DX gas in order to deoxidize the surface, and restore a shiny non-scale surface; the heating is indirect. After 72 hours, the pile of sheets is allowed to cool, and may then be cold rolled again, this time with no reduction (skin roll). The sheet is then inspected under a mercury arc for seams, stretcher strains, buckle, gauge and other particulars.

A part of the hot rolled steel is used as such, for the manufacture, for

^{4a} Thus for number 6, the final mill, 190; number 5, 160; number 4, 108; number 3, 90; number 2, number 1, 46.

^{4b} The length of the rolled sheet may be computed by dividing the proposed thickness in inches by the thickness of the original slab, and multiplying by the length of the slab; width to remain the same.

example, of automobile chassis frames, exhaust pipes, tubes for the differential housing.

THE BESSEMER CONVERTER

Acid Process. The Bessemer converter is a pear-shaped vessel with perforations (the tuyeres) at the bottom through which a blast of cold air (pressure 25 pounds) may be introduced; molten pig iron from a mixer is poured in and blown for a period of about 20 minutes; the silicon and manganese are oxidized and combine with that portion of the iron which is oxidized at the same time. In the simplest case, that of the acid Bessemer process, three periods may be distinguished. In the first, slag forms; in the second, the liquid "boils," the carbon is burned and escapes first as dioxide, later as monoxide (CO); it is the escape of the latter gas which causes the "boil." The flame at the mouth of the converter during the second period is large. The third period is the finishing period, when the last of the

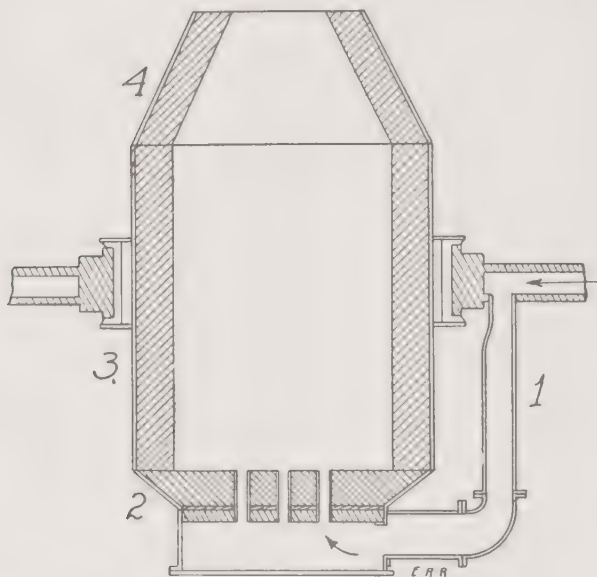


FIGURE 284.—The Bessemer converter for steel; 1, entry for air blast, cold; 2, bottom piece; 3, body; 4, nose piece of the converter. The tuyeres are shown in 2.

carbon burns to monoxide; as its amount diminishes, the flame dies down. Much heat is produced during the blow, mainly by the burning of the silicon (*compare* Problem 2); in fact, the Bessemer conversion succeeds best when there is a 2 per cent content of silicon in the pig iron; with a lower content, 0.8 or 1 per cent, the converter must be kept hot by rapid working. The blow over, an addition of spiegeleisen⁵ is made in the converter, and a short afterblow is applied; the manganese reduces any oxide of iron which has been formed and at the same time furnishes carbon, which the main blow has practically completely removed.

A Bessemer converter for a 10-ton charge is about 15 feet high, mounted on trunnions, and elevated sufficiently to allow the pouring of the finished steel into a ladle. The converter is lined with acid (silica) bricks, and has a removable bottom piece, which lasts only 12 to 15 blows, and a

⁵ Spiegeleisen means mirror iron; it is a low-manganese iron alloy: Mn 15%, C 4%, S, 0.02%, Fe 79.7%, S 0.2%, P 0.28%. The amount added is 6% of the charge, or even more.

removable nosepiece.⁶ Other details are indicated in Figure 284. Converters large enough to hold 20 tons are not uncommon. The charge occupies only one-sixth of the space within the converter, to allow for agitation. The pig iron or melted scrap must contain not more than 0.05 per cent phosphorus.

Basic Bessemer Practice—The Thomas-Gilchrist Process. The basic Bessemer conversion differs from the acid Bessemer just described in several particulars. It is devised for phosphorus-containing pig iron, or melted scrap, and during the blow, it is the burning of the phosphorus⁷ which furnishes the heat, instead of the silicon; the phosphorus content is usually 1 per cent, and may be as high as 3 per cent. Lime is added, in lump form, in order to bind the phosphorus oxide, P_2O_5 , as calcium phosphate; and as such basic material as hot lime would speedily ruin the silica brick lining usually applied to the acid converter, the lining must be different, namely basic. It is made of dolomite bricks. The amount of slag formed in the basic Bessemer is greater than in the acid one, and for the same charge of metal the converter must therefore be somewhat larger. Finally, the spiegeleisen is added only after the metal is in the ladle, so that a reduction of the phosphate by the carbon in the spiegeleisen may be prevented. The basic Bessemer is much used in France and Germany, less in the United States.

The composition of the charge and of the product for the two Bessemer processes are given in Table 97.

TABLE 97.—Composition of charge and product.

	Basic Bessemer Process				Acid Bessemer Process		
	Charge	Steel Per Cent	Undosed**		Charge	Steel Per Cent	Undosed**
Carbon	3.60	0.20	(trace)	3.50	0.20	(trace)	
Silicon	0.61	0.01	(0.005)	2.10	0.02	(none)	
Phosphorus	2.52	0.04	(0.04)	0.04	0.045	(0.045)	
Sulfur	0.07	0.05	(0.05)	0.04	0.044	(0.044)	
Manganese	1.45	0.40	(0.12)	0.45	0.48	(trace)	
Iron	91.75	99.30	(99.7*)	93.87	99.21	(99.8*)	

* Iron oxide is present.

** That is, before correction by spiegeleisen addition.

Both steels given in the table would be mild steels for general structural purposes. The reactions are violent; the pig iron is changed to the pure iron shown under the column "Undosed"; such iron has the fatal defect that it contains iron oxide, which renders the product almost useless. The addition of the ferromanganese or spiegeleisen removes the oxide of iron, for manganese combines with the oxygen of FeO with great rapidity; at the same time, carbon is furnished to reach the designated percentage. That very pure undosed metal is fluid means that a very high temperature is reached in the converter.⁸

It was the invention of the use of spiegeleisen as a deoxidizer and at the same time recarburizer which saved the Bessemer process from failure.

The nosepiece lasts 50 blows; the body, 200.

For heat value, compare Problem 2.

The hotter the iron, the higher its melting point. No fuel is needed in the Bessemer conversion; indeed, before, the heat is due to the oxidation of the silicon (acid process) or the phosphorus (basic process).

in its early days (Mushet, 1856). Other deoxidizers are ferromanganese alloys with 40 to 80 per cent manganese; also silicon alloys and aluminum.

The composition of structural steel need not be those given in the table above; in the case of the towers for the George Washington Bridge over the Hudson, at 178th Street, New York City, the steel used contained about 0.27 per cent silicon. The high silicon content was selected in order to improve the physical properties of the steel, not for the purpose of decreasing any possible corrosion.⁹

Slag. In the acid processes, the slag is due to the burning of the silicon, Si, to silica, SiO_2 , of the manganese, Mn, to the oxide, MnO , and of some of the iron, Fe, to FeO ; these react further to form manganese silicate and iron silicate:

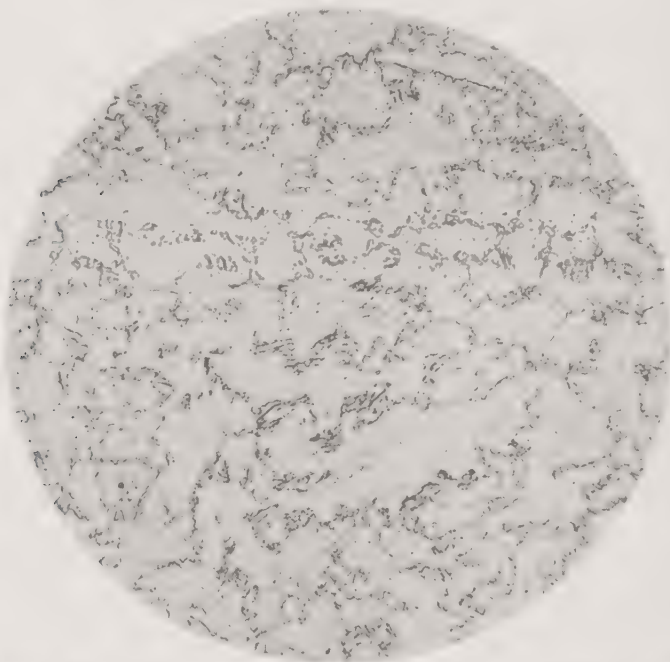
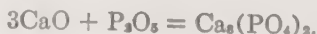


FIGURE 285.—Photomicrograph of regular plain carbon steel, containing 0.27 per cent carbon. After rolling, the steel was annealed at 1250° F. and slow cooled. The background is ferrite, and the lines and curves are spheroidized cementite. 500 diameters. (Courtesy of the Metallographic Laboratory, Bethlehem Steel Company, Buffalo, N. Y.)

In the basic processes, the phosphorus, P, burns to the pentoxide, P_2O_5 ; some iron to its oxide, FeO , and the manganese again to MnO ; there is then formed calcium phosphate,¹⁰ essentially, containing iron phosphate and some manganese phosphate:



The liquid slags are lighter than the melted steel and float on the latter

⁹ Private communication, The Port of New York Authority, Herbert J. Baker, engineer of steel inspection.

¹⁰ For the use of basic slags as fertilizers compare Chapter 18.

Tilting open hearth furnaces are successfully used by a number of plants. A continuous open-hearth process, in which 20 tons of steel are tapped at intervals from a total charge of over 100 tons, is in operation (Talbot); the main advantage is that the bottom of the furnace remains covered by the steel and is not attacked (or very little) by the slag.

Sulfur may be slagged out by means of manganese, which forms manganese sulfide, MnS .

SPECIAL PRODUCTS

Nearly pure iron was made formerly from very pure raw materials, and with charcoal; it is possible to make surprisingly pure irons in the open-hearth process by holding the charge for some time longer in the furnace to lower the content of silicon and manganese; at the ladle aluminum (shot) is added liberally, perhaps $1\frac{1}{2}$ pounds to the ton of iron. The Armco brand of iron, used for cornices and conductor pipes, is such an iron; it rusts either not at all or very slowly; its composition is carbon 0.02 per cent, manganese 0.05, silicon 0.01, phosphorus 0.01.

Steel is iron containing carbon, in part as iron carbide, Fe_3C , called cementite; in part free, as graphite; the total amount for steel lies between 0.05 and 1.5 per cent C.¹¹ Heated and suddenly quenched, it becomes more elastic, harder, and more brittle; these qualities may be varied for any steel by varying the temperature and the period of quenching. In low-carbon steels, most of the iron is free, and occurs as ferrite, of which there are three varieties. By heating to a predetermined temperature and cooling suddenly, the structure existing at that temperature may be preserved, with the properties which accompany it. A steel with 0.89 per cent carbon consists entirely of "pearlite," which is made up of thin parallel plates of cementite and ferrite side by side (a eutectic mixture); above 0.89 per cent carbon, there is a network of cementite around pearlite islands; below 0.89 per cent, ferrite is mixed with pearlite. "Austenite" is a solid solution of carbon in γ -ferrite. The structure of the steel may be studied by means of the metallographic microscope (see illustrations).

Steel is made into a number of forms suitable for certain uses. Several are given in the following list, which has also the quantity in thousands of long tons for the year 1939 (U. S.): rails 1175; track accessories 462; structural shapes 2245; bars: carbon steel 2509, stainless steel 20, other alloy steels 672; concrete bars 1094; plate 2819; sheet: plain and black, 19; strips: plain 748, stainless 33, other 630; skelp 1941; total finished steel 48,132.

In ordinary steels the impurities also affect the properties; manganese makes the steel more elastic, hence more resistant to a shearing force. Molybdenum or tungsten raise the tensile strength; and chromium steel resists attack better than mere carbon steel.

Extra-hard steel may contain carbon only, or manganese 0.5 to 2 per cent with carbon 0.5 per cent and less; or 1 per cent tungsten with 0.5 per cent carbon; or chromium 1 per cent again with carbon 0.5 per cent.

¹¹ Iron with 2.5% carbon and more is pig iron.

Gun barrels¹² are made of chrome steel (1 or 2 per cent) (U. S.); armor plate for battleships (12 in. thick) is nickel-chrome steel (3.3 per cent Ni, 1 per cent Cr), case-hardened. Nickel steel (with 25 per cent Ni) is made in crucibles; the melted steel and melted nickel are poured together into a larger receiver. Nickel raises the tenacity without changing the elastic limit; vanadium has the same effect as nickel and only one-fifth as much is needed. A nickel steel with 3 per cent Ni, 0.40 C, 0.1 Si, 0.60 Mn, deoxidized by aluminum, possesses after heat treatment a tensile strength of 300,000 pounds per square inch; it is ductile and tough. Zirconium, molybdenum, and other elements are also used to strengthen steel.

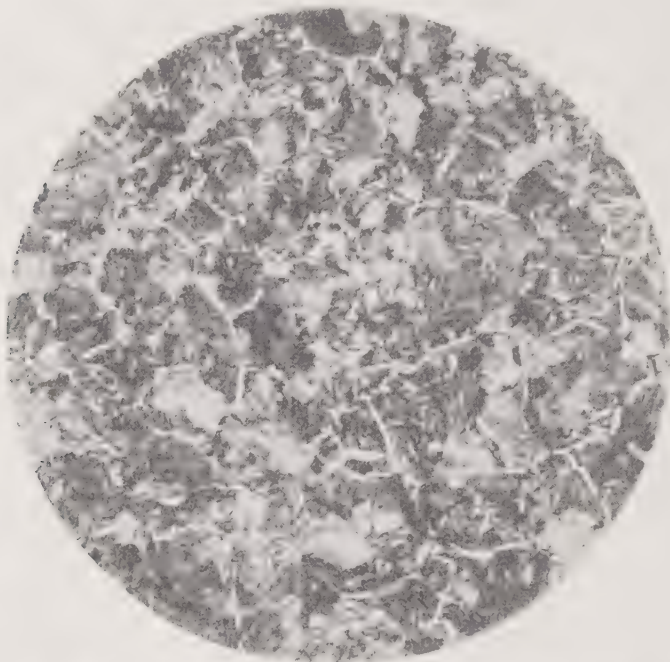


FIGURE 236.—Photomicrograph of a nickel-chrome steel after rolling. The steel contains C .39, Mn .68, P .015, S .018, Si .20, Ni 1.22, Cr .57. The dark areas are pearlite, the white network is due to ferrite. 100 diameters. (Courtesy of the Metallographic Laboratory, Bethlehem Steel Company, Buffalo, N. Y.)

Castings made of steel are presented in Chapter 45.

Self-hardening tool steel, one of the most striking as well as important discoveries,¹³ contains chromium 2 per cent, tungsten 8.5 per cent, carbon 1.85 per cent, manganese 0.15 per cent, silicon 0.15 per cent, phosphorus 0.025 per cent and sulfur 0.030 per cent. It is heated to 940° C., then cooled in a bath of molten lead, and after that, in the air; it is used for cutting tools in the machine shops, and retains its edge even though red hot from the friction of the cutting. Other high-speed tool steels in the past have been high-tungsten steels; for example, the 18-4-1 grade contained

¹² A 14 inch (bore) gun consists of gun proper, inner tube, jacket, hoops and breech-lock pieces. It requires about 2 years to manufacture; it is about 40 feet long. The smaller guns up to 3 inches have tube, inner tube, jacket, and breech-lock. The jacket is forced while hot over the tube (shrink fit).

¹³ By Taylor and White, of the Bethlehem Steel Co.

18% W, 4% Cr, 1% Va., 0.5% Mn, between 0.40 and 0.80% C, balance iron. The effort in the past 12 years has been to substitute molybdenum for the rare and expensive tungsten, and this has been successful. Such a molybdenum high-speed tool steel is the following: 0.80% C, 1.50% W, 1.00% Cr, Va. 1.00%, Mo 9.00%, balance iron.

Columbium in Stainless Steels. Several iron alloys are briefly discussed in Chapter 45, among them stainless steels, which are precious to the chemical engineer because they resist corrosion. When stainless steels are subjected to heat, they become susceptible to corrosive chemicals. A way to preserve the non-corrosive property of the stainless steel consists in adding columbium (F. M. Becket); the columbium¹⁴ combines with the carbon in the steel, and the resulting carbide remains dissolved in the ferrite, in the straight chromium stainless steels, or in the metal, for such alloys as 18-8. The difficulty is thought to have been that chromium carbide formed a carbide which segregated. The amount of columbium added, in the form of ferro-columbium, is about five times its carbon content; to be effective, the carbon content must not be over 0.02 per cent.

Heat Treating. Fundamental to heat treatment is the iron-carbon phase equilibrium diagram, on which temperatures against composition are plotted, and the critical temperature phenomena. To take the latter first: When a piece of carbon steel is heated at a regular rate, it expands continuously until 1350° F. is reached (for a given composition), when it not only no longer expands, but actually shrinks, although the temperature is still rising. By the time the temperature has reached 1475° F., the piece expands again. On cooling the same steel from a high temperature (such as 2600° F.), there is a gradual contraction until 1375° F. is reached, when it stops shrinking, and expands slightly; on continued cooling, at 1225° F., the contraction is resumed. This range is called the critical range, and here it lies between 1225 and 1475° F. The equilibrium diagram marks the limits for the several phases. (Compare the earlier section "special products.")

The critical range differs somewhat for the various steels. All heat-treating operations must have regard for the critical range of the specimen. The various types of heat treating are: 1. Annealing, which means heating above the critical point and holding it there for 24 to 72 hours, then cooling slowly while covered. 2. Normalizing, which is the same as annealing, except that the steel is allowed to cool in air, which is also faster. 3. Quenching or hardening; that is, plunging the steel heated to above its critical point, into a 10 per cent salt solution, or into water, for rapid cooling; or into oil, for medium rapid cooling. Some steels having a high alloy content can be cooled in air. The process of quenching preserves the structure as it is at the high temperature; it produces a high degree of hardness. 4. Tempering, or better, "drawing," which means heating the hardened (quenched) steel to a certain temperature which must not in any case equal or exceed the critical point, and holding it there for some time. Drawing moderates the great hardness produced by quenching, and restores some of the original ductility. Example: A .45 per cent carbon steel quenched

¹⁴For source and method of extraction see Chapter 49.

in water has 600 Brinell hardness; it is heated at 800° F. (427° C.) for one hour per each inch of thickness. The resulting steel has a 444 Brinell hardness. For ordinary work, these drawing temperatures range from 500° F. to 1200° F. (260° to 649° C.).

Several classes of carbon steels, which make up 85 to 90 per cent of heat treated steels, are distinguished, and their susceptibilities to heat treatment differ. Steel with carbon from .03 to .10 per cent (3 point to 10 point) is used for sheets, chain steel, angle iron, and is not heat treated; neither is the next class, .10 to .30 per cent carbon steels, which comprise structural steel and steel which will be case-hardened. Steel with .30 to .60 per cent carbon is the forging grade; it is made into automobile crankshafts, wrenches, and it is heat treated. (Generally, steel with carbon over .40 is for heat treating purposes.) The next class, .60 to .80 per cent carbon steels are for dies, chisels, punches and rails, and is not heat treated; while the following one, .90 to 1.05 per cent carbon, for automobile springs, is oil quenched and heat treated. File steel is 1.15 to 1.30 per cent carbon and is extremely hard.

Case-Hardening. In order to harden the surface while the interior remains soft and tough, steel may be enclosed in a thin case of carbon-rich metal, by heating it while packed in carbonaceous materials. Powdered

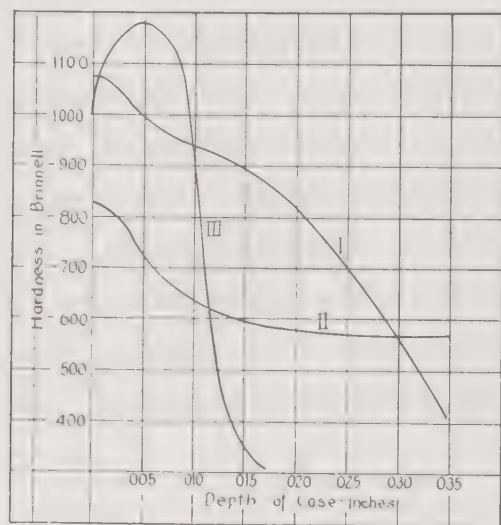


FIGURE 287.—Comparing nitrided steel and carburized steel. I, Cr-Al-Mo steel, nitrided; II, Ni-Mo steel, carburized; III, Cr-Mo steel, nitrided. (From *Metals and Alloys*.)

bone, wood charcoal, charred leather, graphite, anthracite, lampblack, potassium cyanide (fused), sodium cyanide (fused), potassium ferrocyanide, acetylene, propane and other substances are used. The heating is out of contact with the air. The carbon of the packing slowly penetrates into the steel (nickel-steel automobile gears are case-hardened to a depth of 0.040 inch); the steel is usually cooled to a black heat, reheated to a high temperature, and then quenched, in order to temper the case. Balls for bearings are case-hardened, also cams, knives for weighing scales, gears of all kinds, rifle barrels and many other objects. 98 per cent of case-hardened steels are treated as just described.

Case hardening is also accomplished by nitriding, or by a combination of nitriding and carburizing. Nitriding alone is done with ammonia gas in air-tight containers, at elevated temperatures, and with steels of special composition. Case hardening in a cyanide bath brings about both carburizing and nitriding; sodium cyanide or potassium cyanide is always diluted with salt or other inert material, in order to moderate the action.

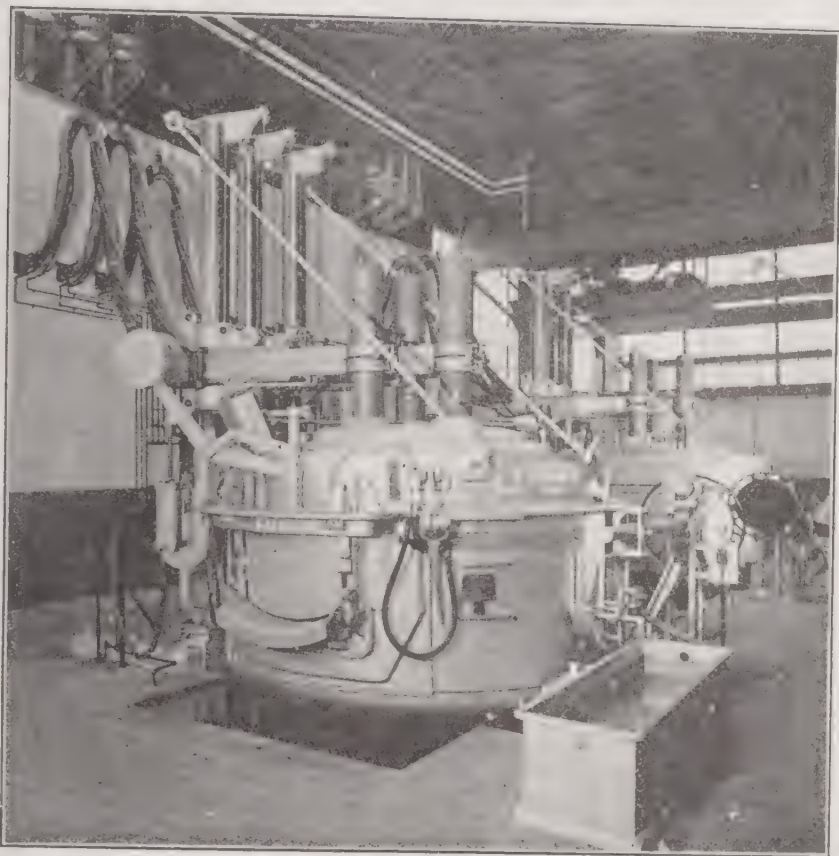


FIGURE 288.—Two Lectromelt furnaces, each of three-ton per hour capacity, of the top charge type. When the charge is finished and ready to pour, the furnace is tilted, and the metal run into ladles. The furnace is righted, the electrodes are lifted, anchoring bolts opened, and the top of the furnace rotated to the left of the reader, exposing the whole of the interior, for easy charging of the next batch. (Furnished by the Pittsburgh Lectromelt Furnace Corporation, Pittsburgh.)

CRUCIBLE STEEL, ELECTRIC FURNACE STEEL

In the cementation process, iron bars of high purity were packed in charcoal, enclosed in a box, and heated for periods of many days. After cooling (also several days), the bars were unpacked and worked in variety of mechanical ways in order to make them homogeneous. The product was a high carbon steel, at that time the hardest (after suitable tempering) available. This lengthy process was superseded by the crucible

process, in which a steel of uniform composition could be made in less time. Melting the steel offered the additional advantage that additions other than carbon could be made, such as other metals, which had the property of hardening steel. The crucibles have in turn been displaced by the electric furnace, which may be considered rather a large crucible in which heat is applied directly to the charge, by the conversion of electrical energy to heat, and need not pass through the walls of the crucible.¹⁷

The capacity of the steel furnace is not large; it runs from 1200 pounds to as much as 6000 pounds (tool steel) at one pour. A coreless induction furnace has been found well adapted to melting cobalt high-speed steel, tungsten high-speed steel, heat-resisting alloys, corrosion-resisting alloys and special compositions for tool and magnet steel. A number of special alloys are listed in Chapter 45.

The materials charged are selected scrap, flux, deoxidizers, muck bar (a very pure steel), ferro-tungsten, for example, and other alloys.

It is essential to make a distinction between structural steel and crucible steel; the former is made in huge quantities, and sells under 10 cents a pound, while the latter is made in small lots, and brings 80 cents a pound.

Ferro-Alloys. A number of ferro-alloys are made in considerable quantities. Ferro-manganese and its lower grade, spiegeleisen, are made in the blast furnace from manganese-bearing ores. The stronger grades of ferro-silicon, perhaps the most important ferro-alloy, are made in the electric furnace; ferrochrome, ferrotungsten, and ferromolybdenum also. The lower grades of ferrosilicon, up to 10 per cent, are made in the blast furnace, by increasing the coke ratio. Ferrovandium is made in the electric furnace; ferrotitanium is made to some extent by the thermite process, but mainly in the electric furnace.¹⁸

There were produced in American furnaces in 1939 783,615 long tons of ferro-alloys valued at \$81.1 a ton; in 1940, 1,115,500 long tons valued at \$111.5 a ton.

Comparison. The relative importance of the various processes is shown by the percentage production in each. The total steel production in 1940 (U. S.) was 66,982,686 net tons, of which 90.8 per cent was made in the basic open hearth, 1.4 per cent in the acid open hearth, 5.5 in Bessemer converters, 2.6 in electric furnaces, and a very small amount in crucible furnaces. Alloy-steel ingots and castings are included in the grand total, and formed 7 per cent of it.

The average price for all types of finished steel for 1939 was \$50 a net ton.

OTHER PATENT

U. S. Patent 1,786,322, electric furnace for melting metal.

¹⁷ The Stassano, Keller, Girod, and Heroult furnaces are discussed in *Electrochem. Met. Ind.* 7: 255 (1909), with illustrations. See also Chapter 4 on the steel furnace, in "The steel foundry," J. F. Hall, New York, McGraw-Hill Book Co., 1922.

¹⁸ "The ferro-alloys," J. W. Richards, *Ind. Eng. Chem.*, 10, 851 (1918). An up-to-date discussion of ferro-alloys will be found in the chapter on "Metals and Ferro alloys used in the manufacture of steel," by W. J. Priestley, pp. 615-621, in "Metals Handbook," 1936 ed., Cleveland, O.

PROBLEMS

1. A charge of metal for a basic open hearth furnace weighs 225,000 pounds and contains 1.4 per cent silicon; the metal tapped weighs 200,000 pounds and contains 0.04 per cent Si. All the silicon has formed calcium silicate CaSiO_3 . How much calcium silicate is obtained?

The corresponding figures for phosphorus are 0.1 per cent in the charge and 0.02 per cent in the metal; calcium phosphate is formed, $\text{Ca}_3(\text{PO}_4)_2$. How much? In the basic open hearth, no lime is added; the silica forms iron silicate with the iron oxide. FeO ; using the figures given above for silicon, and assuming enough ferrous oxide to be formed, how many pounds of iron silicate would be formed?

2. A 10-ton charge in a Bessemer converter has the composition given below: C 3.50 per cent; Si 2.10; P 0.04; S 0.044; Mn 0.48. Right after the blow, before any addition is made, the steel contains no carbon, no silicon, no manganese, while the phosphorus and sulfur content are unchanged. From the heats of combustion below, compute the number of B.t.u. evolved; and comparing Chapter 12, find the weight of coal which would be equivalent to this amount of heat.

1 pound of silicon	on burning to SiO_2	evolves 12,700 B.t.u.
1 " " phosphorus	" " " P_2O_5	" 10,700 "
1 " " manganese	" " " MnO	" 3,000 "
1 " " carbon	" " " CO	" 4,409 "

NOTE: For other problems consult "Metallurgical calculations," in 2 vols. by Joseph E. Richards, New York, McGraw-Hill Book Co., 1910; steel problems are in vol. 2.

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The iron-carbon-temperature diagram will be found on p. 140, in "The Phase Rule," Alexander Findlay, London and New York, Longmans, Green and Co., 1927, or on p. 253 in the "Metals Handbook" for 1936, or on p. 438 in "The metallography and heat treatment of iron and steel," Albert Sauveur, Cambridge, Mass, Sauveur and Boylston, 1916.

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The study of metals involves the application of several sciences. The extraction of the metals from their ores, and the finding of the ores, is the task of metallurgy. In explaining the origin of the ores, metallurgy leans on geology; in choosing the reactions for the extraction and refining of the metals, the metallurgist applies chemical science. An important branch of metallurgy is metallography, the study of the internal structure of metals and alloys.

Chapter 49

Copper, Lead, Zinc, Tin, Mercury

The metals copper, lead, zinc, tin, and mercury form a middle group of metals, more expensive than steel and iron, but cheaper than the precious metals. They may be described as base metals, because they are relatively easy of attack by acids and reagents, and because they form the oxide when heated in a blast of air. The precious metals remain unaffected under such conditions; in fact, silver is rid of lead by oxidizing the latter. The relative importance of copper, zinc, and lead is shown by the table below,¹ which also indicates what portion of the metals are produced in the United States. Mercury is less important and will be treated separately; nickel and tin are discussed further on:

TABLE 98.—*Production of copper, lead and zinc (in short tons).**

	1940 (U. S.)	1939 (U. S.)	1939 World
Total new copper	1,008,785	714,873	2,443,000
Total new and old copper	1,541,000	1,215,000
Primary zinc	675,275	507,236	1,802,000
Primary and secondary zinc	724,192	557,664
Primary lead	533,179	484,035	1,919,000
Primary and secondary lead	793,479	725,535

* Minerals Yearbook.

It will be noted that for each metal, a considerable part comes from the United States; the proportion is likely to remain the same in the future except for copper, which may be produced extensively in Africa. The production of mercury is decreasing in the United States, while the Italian and Spanish productions are increasing. The nickel refined in the United States chiefly from Canadian ores, while the tin is from ore shipped in from the Malay Peninsula.

Compared with steel, these productions are small, but the uses of these metals are so specific that it would be difficult to do without them. It is interesting to note that copper serves to transmit² the electrical current, and to collect it at the generator; zinc serves in dry cells; while lead is the metal used in storage batteries; hence all three are closely connected with electrical practice. Other uses of the metals and their alloys will be found at the end of the chapter.

¹ and other tables in this chapter, Minerals Yearbook, review of 1940, Bureau of Mines.
² well suited for power transmission.

COPPER

Copper, the red metal, occurs in the native form only in the Upper Peninsula of Michigan; the shafts are deep (5000 and 6000 feet). A number of blocks of the metal have been found which are so large that they cannot be brought to the surface through the shaft; and they cannot be dynamited to smaller fragments because the metal is soft enough to yield, preventing fracture. Other copper fields have combined copper, mainly as sulfides, but also as carbonates and silicates. Examples are chalcopyrite, $\text{Cu}_2\text{S} \cdot \text{Fe}_2\text{S}_3$; bornite (peacock ore), $3\text{Cu}_2\text{S} \cdot \text{Fe}_2\text{S}_3$, richer in copper (55 per cent); chalcacite, Cu_2S , with 80 per cent copper; azurite, and malachite,³ $\text{CuCO}_3 \cdot \text{Cu}(\text{OH})_2$, carbonates; chrysocolla, a silicate. Malachite is of an intense green color; azurite and chrysocolla are blue. When the ore occurs in veins, a high-grade material is obtained, with 8 to 12 per cent Cu; but low-grade ores are also profitably mined and worked to as low a content as 1 per cent. The principal producing countries are indicated in the table below:

TABLE 99.—*Copper production in metric tons (Smelter).**

	1939	1940
United States	698,323†	922,369†
Africa	351,803
Chile	324,591	337,021
Canada	229,370
U. S. S. R.	144,000
Japan	104,000
Germany and Austria	66,000
Mexico	44,300	34,400
Yugoslavia	41,658	42,951
Peru	34,115	33,584
Total	2,216,000

* Minerals Yearbook.

† Exclusive of scrap.

Within the United States, the production in 1940 in the several States and territories would allow the following order, for tonnage produced: Arizona 31.6%, Utah 27.36, Montana 14.20, Nevada 8.65, New Mexico 7.75, Michigan 5.03, Colorado 1.45, Washington 1.16. The Montana ores (Anaconda) are high-grade sulfides; in the Miami district in Arizona, the ores are low-grade sulfides. Nevada (Ajo) has azurite and malachite, and the mines are of the open pit type. Some of the Arizona copper mines are shaft mines, and others open pit mines (Jerome); Bingham in Utah is an open pit mine.

Concentration of the Ore. The high-grade sulfide ore, with 2 to 8 per cent copper, is concentrated by floating off the lighter gangue and rock with flowing water, in classifiers such as the Dorr, in jigs or on shaking tables with grooves; the jigs are the older devices and are being displaced by the classifiers. A preliminary crushing gives the desired size. For low-grade ores, the crushing in jaw crusher⁴ or gyratories⁴ is followed by pulverizing in ball mills⁴ to pass (90 per cent) through a 40-mesh screen. After screening, the fine material sometimes receives the "coating oil," with which it

³ The Egyptians used malachite for carvings.

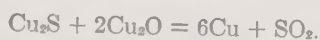
⁴ Chapter 44.

is intimately mixed; the oiled powder next passes to the flotation machines, with either paddle or air agitation. More generally, the ore receives no preliminary oil treatment. The flotation machine contains the "frothing oil" suspended in water; the emulsion so formed has a selective action on the crushed ore; the sulfides are lifted into the froth, while the worthless material sinks. The lifting is done by a bubble of air which adheres to the oil-moistened particle and carries it up. The froth overflows to rotary suction filters which deliver a cake of concentrated ore, dry enough to be sent to the smelter. The flotation machine is small, and batteries consisting of many units are used.

The oil which serves for flotation is usually creosote oil. The amount is surprisingly small, perhaps one quart to a ton of ore. Besides the creosote oil, pine oil, certain coal-tar oils, kerosene acid sludge from the refineries, and a few others, are suitable. Mineral salts and organic substances are also added, with the oil.

Without the flotation system, it is doubtful if low-grade ores could be profitably extracted.

Smelting of the Concentrated Sulfide Ore to Crude Copper. The concentrated ore is placed on the hearth of a reverberatory furnace⁵ and heated with free access of air. Sometimes the ore is first melted and cast into pigs, and these fed to the furnace. As the melting progresses, a part of the sulfide becomes oxidized, and the oxide acts on unchanged sulfide, liberating the metal and forming sulfur dioxide gas. The mass has melted by this time, and the metal sinks to the hearth; it is tapped at intervals. Flux is added in order to bind siliceous admixtures, and the slag which thus lies at the surface. The reaction between the oxide and the sulfide is violent and audible:



The product of this operation is crude copper, called blister copper, because it has cavities due to escaping gases. The blister copper is cast into anode sheets for the electrolytic refining. Blister copper is about 98 per cent Cu; it retains any gold or silver which the ore contained.

There is another way to make crude or blister copper, consisting of two steps. First the ore is charged into the rectangular blast furnace (24 to 30 feet long, 4 feet wide) with coke and flux, and there melted; the copper sulfide remains sulfide, but the gangue is removed as a slag, so that the result is really a purification of the copper sulfide, now called the "matte." It is tapped at intervals, and used while still hot in the next step, the Bessemer converter. The slag is also tapped at a special taphole.

The hot melted sulfide is fed to a small converter (1 to 3 tons) resembling the Bessemer for steel⁶ with, however, an important difference: the tuyeres are in the side of the converter, high enough so that the metal does not drop below them and escapes the oxidizing action of the blast. A small amount of acid flux is added, and the blowing performed. Sulfur dioxide escapes, and the metal sinks below the tuyeres; as the heat evolved is not so high as in the steel converter, the metal is less fluid, and this con-

⁵ Chapter 4.
⁶ Chapter 48.

struction prevents the choking of the tuyeres. The converter is discharged by tipping. The iron impurities are oxidized and form silicates with the acid lining of the converter, or with the flux.

The tendency is to combine the two steps, blast furnace followed by the converter, into one, by melting in the converter itself (horizontal cylinder) and then blowing the melted sulfide.

Certain ores are adapted for treatment by the two-stage pyritic method, in which a saving of fuel is effected by using the heat of combustion of the iron pyrite which they must contain; a copper matte is produced which is made into blister copper in one of the ways described above.

There are many variations in the smelting of copper sulfide ores; in many cases a preliminary burning off of much of the sulfur, called roasting, is a separate process. It is performed in rotary shelf burners, similar to the Herreshoff furnace described in Chapter 1; or in the Dwight-Lloyd sintering machine, in which an endless belt made of cast-iron buckets with perforated bottoms pass over a strong suction box after their ore contents have been ignited by an oil flame.

Wet Methods of Extraction. The methods just given apply to sulfide ores only. Azurite and malachite may be extracted by the sulfuric acid-leaching process; a solution of copper sulfate results from which the copper is precipitated partly by electrolysis, the rest in powder form by old iron (Ajo district in Nevada). This might be called the acid-leaching method.

The ore (1.3 to 2 per cent Cu) is dumped into tanks 88 feet square, 17 feet deep, made of reinforced concrete, with wooden bottoms, and leached 8 days on the countercurrent principle. The copper sulfate liquor with 2.985 per cent Cu is passed into the electrolytic deposition cells, with (impassive) lead anodes, and copper sheet cathodes, on which latter the liquor deposits a part of its copper; the outgoing liquor with 2.513 per cent Cu and a gain in sulfuric acid is strengthened by further leaching and reaches the cells again; this is continued until the impurities have accumulated so much that the liquor must be discarded. The remaining copper is then precipitated by scrap iron.⁷

In the early days of copper mining in Michigan, the tailings, still containing an appreciable percentage of copper, were washed into the lake from the stamp mills; now that the mine shafts must be deeper than formerly, operation costs have risen and it has become profitable to work over the discard of former days. This is done in part by concentrating by means of classifiers and shaking tables, the remainder by leaching with an ammonium carbonate solution.⁸ Acid leaching would not do, for the gangue is mainly calcite, which would consume the acid.

The old discard from the stamp mills, with 0.8 per cent Cu, is brought up from the lake bottom by sucker dredges, screened twice, and classified. The Dorr classifier, for example, is of the drag type. It consists of an inclined trough in which scraper blades move in the sand toward the

⁷ "First year of leaching by the New Cornelia Copper Co.," Henry A. Tobelmann and James A. Potter, *Am. Inst. Mining Eng. Bull.*, No. 146, 449 (1919). Compare also the article by William F. Greenawalt, "The Greenawalt electrolytic copper extraction process," *Am. Inst. Mining Met. Eng.*, 70, 529 (1924).

⁸ "Ammonia leaching of Calumet and Hecla tailings," C. H. Benedict and H. C. Kenny, *Am. Inst. Mining Met. Eng.*, 70, 595 (1924).

upper end, returning to their first position while raised and outside the sand. A stream of water carries down the lighter particles which the blades dislodge, while the heavier particles are pushed up along the floor and are finally discharged at the upper end. This upper discharge called the "sands" and richer in metal now, is ground in a Hardinge⁹ mill, concentrated, and the concentrated portion sent to the smelting furnace. The weak tailings after suitable classification and concentration reach the leaching tanks. These are steel tanks 54 feet in diameter, 12 feet high, provided with covers; the contents of such a tank are percolated with the ammonium carbonate solution for 72 hours. At the end, the copper solution is evaporated in tank-like stills, the ammonia recovered and used again, while the copper is left behind in the form of oxide. The residue in the leaching tank is washed and returned to the lake.

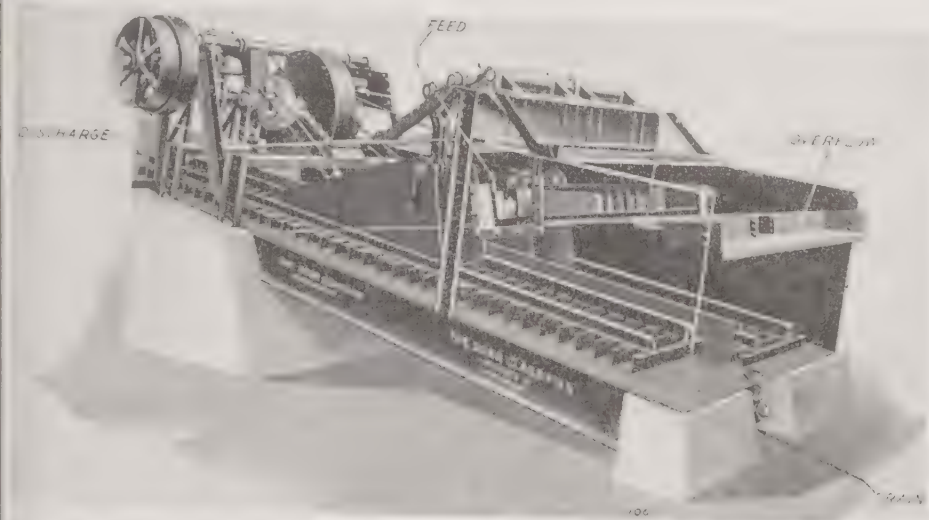


FIGURE 28Sa.—The Dorr classifier, with inclined trough, rakes which sweep up, then are lifted out by a cam for the return stroke. (Courtesy of the Dorr Co., Inc., New York.)

The chemical action is as follows: Cupric ammonium carbonate with excess ammonium carbonate dissolves native copper in the old discard, to form cuprous ammonium carbonate. This latter solution is the one which is distilled. The solution of cupric ammonium carbonate required for the extracting solution is obtained by treating a portion of the cuprous ammonium carbonate solution with air.

Still another wet extraction method which deserves brief mention is the one practiced at Rio Tinto, in Spain. The iron pyrite mined there contains 1 per cent copper. It is extracted by oxidation of the copper glance, Cu_2S , and washing out the copper sulfate formed. The ore is piled in heaps 10 feet high containing 100,000 tons; draft pipes are built into the heap, and the top has grooves and basins for the distribution of water. The wash water is passed over pig iron, which precipitates the copper metal.

⁹ Chapter 44.

One-half the copper in the ore is washed out in 3 months, 80 per cent of the other half in 2 years. The ore is called washed when the copper content has been reduced to 0.3 per cent. The oxidation of the copper sulfide is due to the action of air and of ferric sulfate.

Electrolytic Refining of the Crude or Blister Copper. The crude copper with 98 per cent Cu is made into pure copper by electrolysis in a solution of copper sulfate kept slightly acid by sulfuric acid additions. For many years, the native lake copper was quoted one-eighth cent higher than electrolytic; lake copper is very pure, and very small amounts of impurities affect the properties of the metal to a considerable extent; it is now generally recognized that electrolytic copper made from sulfide and other ores is the equal of native or lake copper. The blister copper is cast into anodes, flat sheets 3 feet long by $3\frac{1}{2}$ feet wide, and three-quarters of an inch thick; these are suspended at a distance of 2 inches from the cathode, a copper sheet of similar dimensions except that it is as thin as paper (0.01 inch). The direct current passes through the solution; the anode decreases in thickness, while the cathode gains. During the transfer of the metal, the impurities are removed in various ways. The noble metals, silver and gold, drop off as the copper disintegrates, and deposit as the anode mud, worked up later into the precious metals. Nickel, cobalt, iron and zinc dissolve and remain in the solution; lead and bismuth form a sulfate mud; arsenic forms an insoluble arsenate with copper, and also drops into the mud. Every time an anode is replaced, the muddy liquid is pumped out.

By maintaining the proper voltage, none of the impurities plate out with the copper, hence its purity. The current density is 15 amperes per square foot of surface, the voltage 0.3 to 0.35 per plate, and the temperature 130°F . The electrolyte is circulated and periodically changed in order to remove the gradually accumulating soluble non-copper salts.

The cathode plates are remelted and cast into ingots.

LEAD

The important lead ore is galena, the sulfide, PbS , a black ore which is sometimes found well crystallized; its purity varies in the different deposits. Lead is also obtained from a mixed lead and zinc sulfide, and this in addition may contain silver. The production for the different countries is given in Table 100.

TABLE 100.—*World production of lead (in metric tons).**

	1939	1940
United States	404,257	468,675
Australia	269,590	
Mexico	219,300	195,071
Canada	172,880	
Germany-Austria	181,440	
Belgium	82,000	
Burma	77,220	
France	42,000	
Italy	38,000	
Total	1,741,000	1,700,000

* Minerals Yearbook.

In the production of lead, the United States leads; for the several States, the figures are as listed in Table 101.

TABLE 101—*Min. production of recoverable lead, by districts (U. S. (in short tons).*

	1939	1940
Southeastern Missouri	153,522	169,908
Coeur d'Alene region, Idaho	81,699	95,609
Bingham, Utah	36,842	37,857
Jonlin region, Ka. Mo., Oklahoma	44,176	35,311
Park City region, Utah	11,631	19,749
Total	413,979	457,392

Two-thirds of the Missouri production of lead is from the southeastern portion of the State, where galena is found; the other third is from the southwestern part of the State, an area rich in zinc blende and lead-zinc sulfides; the main product in this area is zinc. The southwestern district is described in more detail under zinc, in the next division. Near Leadville, Colorado, the ores mined are mainly lead-zinc sulfides, carrying silver. The method of extraction for galena ores includes a crushing and screening followed by classifying in a Dorr classifier or a similar device. The classifier delivers at one end the "sands," at the other, the "slimes." The sands are concentrated further on shaking tables, which yield concentrated ore, ready for smelting, and tailings which are treated further for pulverizing in a ball mill. The concentrated ore may be 60 to 70 per cent Pb, from an original ore 6 to 8 per cent Pb.

The slimes are thickened in a Dorr thickener and filtered, yielding a cake containing 60 per cent Pb.

The concentrated ore is smelted in a square blast furnace not over 10 feet high, or on a hearth; an improved form of the latter is the Newnman hearth, much favored in Missouri.

A simpler hearth for lead smelting is a shallow cast-iron box in which fuel, and flux are placed, while the blast is applied from the rear, upward. The hearth is similar to an ordinary blacksmith's forge. The metal reaches the bottom and is siphoned off. Fresh ore and fuel are spread constantly, and the mass is rabbled by hand. In the Newnman hearth, rabbling is mechanical; its size is 8 feet in length, 20 inches wide and 8 inches deep, and its capacity is over three tons of lead produced in 8 hours.¹⁰ In the blast furnace, the ore mixed with the flux, which may be iron ore and lime, and with coke as fuel, is fed in. Lead in the liquid form collects at the base and retains any silver or gold which the ore contained. The lime displaces the lead in any lead silicate which might have formed, while the iron oxide binds the sulfur which fails to burn off as sulfur dioxide, forming iron sulfide. The lead and slag are tapped at different levels, very much as is done with pig iron in the iron blast furnace. The iron oxide used in the charge is generally cinders from iron pyrite from the sulfuric acid plants.

When silver is absent, the first product is freed from antimony, tin, copper, zinc, sulfur, and iron, present in small amounts, by melting the product and maintaining it at red heat in a reverberatory furnace. The

impurities as oxides (except zinc) mixed with lead oxide (litharge, PbO) form a skin on the surface which is removed from time to time; to facilitate the removal, some lime is added, which stiffens the oxides. The zinc oxide passes off in the fumes.

If silver is present in small amounts, it is removed by melting the lead in one of a series of pots and allowing it to cool slowly; the lead, free from silver or poorer in silver, separates as crystals which float at the surface, leaving the silver-containing lead, or richer lead, in the molten state. The crystals are ladled into the pot on the left, the melted lead into the pot on the right. The operation is repeated, until on the left lead free from silver is obtained, while on the right a lead rich in silver is collected. This process is known as the Pattinson process, which is used in Great Britain and on the Continent.

The silver-rich lead may be concentrated in another way, namely by adding melted zinc, which alloys with silver (gold at the very first, if any present) and forms a scum which contains the silver, leaving a melted lead poorer in silver. The separation of the silver is not complete, and must be repeated several times. The scum is distilled for zinc in graphite retorts, leaving lead and silver; this is treated for the recovery of the silver as described in the next chapter under silver. The zinc process is called the Parkes process and is the standard process in the United States. There is a variety in the details of treatment in the various plants, designed to suit the particular ore treated.

The lead free from silver may now be purified in a reverberatory furnace, as described three paragraphs back.

A somewhat different procedure is the Harris process, in which crude melted lead is agitated with molten caustic ($NaOH$), which removes all the undesirable metals, including arsenic, but does not affect the lead nor the silver. The purified lead is then desilverized.

A portion of the lead production, perhaps one-quarter of the total, is consumed in making white lead and other pigments.¹¹

It has been estimated that the increased demand of the country for tetraethyl lead to be added to gasoline for all purposes, defense and civilian, would require 73,000 tons of lead in 1942. The 1940 and 1941 production rate called for 52,000 tons.

Quality of Ores. When copper is present in an ore forming part of mixture smelted in the lead blast furnace, the aim is to recover it in the form of matte (copper sulfide), which forms a middle layer, with the slag over it, the melted lead under. The matte forms only if enough sulfur is present.

Zinc is not recovered in the copper nor in the lead-smelting operations, but passes to the slag in part, and to the fumes. Over 10 per cent of zinc in the slag makes it viscous, decreasing furnace capacity; in the fumes, the zinc increases losses by volatilization. There is therefore a penalty of 30 to 50 cents for each per cent zinc above 1 per cent per ton. This heavy penalty has stimulated efforts to separate zinc blende from

¹¹ Chapter 31.

lead or copper before selling the ores to the smelter.¹² There is a bonus on iron because it fluxes out the silica without requiring the addition of purchased limestone. There is a penalty (light) for silica above a certain percentage.

ZINC

The zinc ores of industrial importance are the sulfide, ZnS , called zinc blende, and the carbonate, called calamine. The sulfide is white when pure, but the ore is generally brown or black from admixed iron or lead. The mixed sulfides of lead and zinc are also used, for both their

TABLE 102.—*World smelter production of zinc, by countries where smelted, in metric tons.**

	1939	1940
United States	460,154	630,740
Germany	212,285
Belgium	185,700
Canada	159,338
Poland	117,936
Australia	72,363
France	60,262
United Kingdom	50,440
World	1,635,000

* Minerals Yearbook.

etals. Zinc blende is more important than calamine. To these may be added franklinite, a double oxide of iron and zinc, and willemite, a zinc silicate, both found at Franklin, New Jersey, and actively mined.

The output of spelter (zinc metal) in the several countries is given in Table 102; in a general way, the figures also indicate the production of zinc in the countries named.

It will be observed that the United States retains the lead in zinc production which it has in lead and copper; the two countries next in importance have not appeared in the list of copper producers, and only one, Belgium,¹³ appears in the list of lead producers, in the seventh place.

TABLE 103.—*Mine production of recoverable zinc, by districts (U. S.) (in short tons) (Minerals Yearbook).*

	1939	1940
Joplin region, Kansas, Missouri, Oklahoma....	224,446	232,437
New Jersey	88,716	91,406
Coeur d'Alene, Idaho	40,065	62,948
Summit Valley (Butte), Montana	20,016	35,899
St. Lawrence County, New York	36,014	35,686
Eastern Tennessee	56,225	34,796
Central New Mexico	23,677	29,573
Bingham, Utah	20,861	21,812
Total	491,058	589,988

Within the United States the order is also quite different; in Table 103, the mine production of zinc ores, calculated to zinc metal, is stated.

The mine production does not quite agree with the spelter production because there is a loss in smelting, and because ores are stored and

¹² *Eng. Mines Tech. Paper No. 83*, Ch. H. Fulton (1915).

¹³ The main mine is the Moresnet, on the German border; it has yielded calamine, blende, and has for many generations, and has been in continuous operation since the 15th Century (Vieille Montagne Company).

worked up perhaps a year later. The tri-state district is placed together because, although part of three States, it is geologically a single deposit. Its area is only some 10 or 15 miles square; it lies in three contiguous counties, Ottawa (Oklahoma), Cherokee (Kansas), and Jasper (Missouri), of which Ottawa County is at the present time the best producer. Joplin lies in the district, in Jasper County. As the table shows, this district is the prime producer in the United States. The ore is mainly zinc blende.

After crushing, the ore is concentrated in jigs, shaking tables,¹⁴ and by oil flotation; still another device sometimes used for zinc ores is the electrostatic separator.^{14a} The concentrated ore is roasted in rotary shell burners, which are the prototype of the rotary burner used for iron pyrite burning¹⁵; the sulfide is thus transformed into the oxide. The reduction of the oxide to the metal is performed in rather small, horizontal fireclay retorts, banked over each other, and set in a furnace receiving preheated gas and air; in this way, a high heat is applied to the retorts, and the metal formed within them is distilled into the fireclay receiver placed at the mouth of the retort. The volume of the retort is 1.5 to 1.9 cubic feet, which is filled with finely divided oxide mixed with 25 per cent non-caking coal. The receiver is capped by a third piece, the condenser, in which the first vapors of the metal condense as a dust (zinc dust); receiver and condenser have an opening through which the carbon monoxide formed passes out; it burns at the outlet from the condenser. The charge for a retort is 40 to 50 pounds of oxide. The metal for the main part collects as a liquid in the receiver, and is removed by a ladle. The number of retorts in the United States is 62,368 (1940), distributed in 17 plants, perhaps 60 to a furnace for the largest furnaces.

In the case of ores containing both zinc and lead, with the zinc above 10 per cent, the practice is to work the ore in the retorts for zinc, as described above. The residue is then handled as a lead ore would be. With the zinc below 10 per cent, the ore is worked for lead, and the zinc passes out as oxide in the fumes.

Electrolytic Zinc. Just after the war of 1914-18, electrolytic zinc was a curiosity; since then the demand has steadily increased. Of the United States production for 1940, 27.5 per cent is electrolytic zinc, 72.5 per cent is distilled zinc; outside the United States, 43 per cent of the production is electrolytic. Electrolytic zinc sells at 4 cents above the market for spelter, yet in spite of that, it is bought; the reason is that its high purity, 99.999 per cent, gives it superior properties, particularly corrosion-resisting qualities. Its high purity is primarily the result of the necessity of having the deposition bath absolutely pure, if any zinc is to be deposited at all.

The roasted ore is dissolved in the spent acid from the cells, iron added to remove arsenic and antimony, manganese dioxide (if not present in the ore) to oxidize the iron, zinc oxide to precipitate the iron, and zinc metal to remove copper, cobalt, and nickel. The resulting pure solution is then electrolyzed.

¹⁴ Chapter 50.

^{14a} Sutton, Steele, and Steele, *Manufacturing Engineers*, Dallas, Texas.

¹⁵ Chapter 1.

Indium Extraction. Indium occurs in many zinc ores, and may be isolated by using the following sequence of operations: ^{15a} the ore concentrate, mainly sulfides, is roasted (at 400 to 600° C. (752 to 1112° F.)) to produce a calcine, mainly oxides. The calcine is leached in a series of Pachuca tanks with sulfuric acid. The solution carries Zn, Fe, Au, Ag, As, Sb, and substantially all the indium. The acid solution receives calcium carbonate in the last tank, which causes the separation of In, some Fe, Au, Ag, Cu. This precipitate is now treated in other Pachuca tanks with acids, with air agitation. The metals redissolve. The solution is now treated with zinc metal, so that In, Au, Ag, Cu separate in the metallic form. These solids are treated next with 25 per cent sulfuric acid for 1½ hour, and the solution so obtained receives hydrogen sulfide, which throws out Au, Ag, and Cu as sulfide, but not the indium. The slurry is filter pressed, the filtrate blown free of hydrogen sulfide, and sent to the electrolytic tanks, where the indium is plated out, practically pure.

Moistening the ore concentrate with sulfuric acid, and roasting this wet concentrate at 1100 to 1250° F. (593 to 677° C.) leads to increased yields of indium. ^{15b, 15c} (See under Silver in Chapter 50.)

Another method provides for the recovery of indium (and gallium) from the lead-containing retort residues in the zinc distillation process. ^{15d}

TIN

Tin until 1939 was smelted mainly in England, in Holland, and in the Netherlands Indies (Batavia). In 1941, the Defense Plant Corporation ordered a smelter erected at Texas City, Texas; the smelter was constructed and is now operated by the Tin Processing Corporation, a subsidiary of the N. V. Billiton Maatschappij of Batavia. The capacity is 18,000 tons of fine tin a year. The normal U. S. consumption per year is 75,000 tons. The new smelter is well situated to use Bolivian ores. The world production in 1940 was higher than for 1939, in response to war and defense demands, and came to 231,700 long tons.

The main producing countries of tin minerals, mainly tinstone, in normal times, are the Malay States 85,384 long tons of tin in the ore; the Netherlands Indies 44,447, and Bolivia 37,923; world total 206,400 (1940).^{*} The metal is obtained by reducing the ore, which is generally the impure oxide, SnO_2 , with coal on the hearth of a reverberatory furnace. The crude metal so obtained is refined by placing it, after solidification, in the furnace and heating gradually, so that the melting is slow; the first metal is the purest; this system is called liquation, and is used for some of the other metals also. A further refining is by melting the metal in a pot, and suspending it poles of green wood; the gases formed agitate the metal, and the impurities oxidize, forming a scum which can be removed. Poling is used for other metals also.

^{15a} U. S. Patent 1,847,622; see also 1,839,800.

^{15b} U. S. Patent 1,912,590.

^{15c} Silver-indium alloys are presented in Chapter 50.

^{15d} U. S. Patent 1,855,455; 1,886,825.

^{*} Minerals Yearbook.

MERCURY

The chief ore used for the extraction of mercury is the sulfide, Hg₂S, cinnabar, a red ore. The chief United States producer has been California (the New Idria mine in San Benito County).

TABLE 104.—*World production of mercury in metric tons.*

	1929	1932	1935	1939	1940
United States	817	435	595	642.3	1,302.3
Spain (Almaden)	2,476	816	1,227	1,842
Italy	1,998	1,016	878	2,315
Mexico	83	253	216	254.3	401.7
Total	5,610	2,850	3,330
Total for 1938—5,113.7					

The production for mercury is usually given in terms of flasks (made of cast iron) of 76 pounds each. In the arts, mercury is used less than formerly. It is still used in countless ways of semi-scientific nature, but in amounts very small. A considerable use remains in dental fillings, and even this use will call for less new metal than formerly (at least in proportion) now that the mercury from the waste amalgam is recovered. Mercury is consumed for the manufacture of mercury fulminate, which has held its place for the explosives of war as well as peace explosives. It is this demand which has stimulated the production. Mercury as the working substance in boilers and turbines is presented in Chapter 12.

Cinnabar is roasted; the free metal and sulfur dioxide form. They pass together into a series of chambers where the velocity of the gas is reduced; the mercury deposits, while the sulfur dioxide passes out. The partly cooled gases may also be passed through small air-cooled glass condensers (aludels). The metal may be refined by distillation. Mercury alloys with many metals, to form "amalgams," but not with iron; the metal it attacks easiest is gold.

NICKEL

Almost no nickel is mined in the United States.¹⁶ The world production in 1938 was 115,500 metric tons of nickel metal, of which 95,514 tons were produced in Canada. In 1939, Canada produced 102,559 m. tons of nickel. The second big producer is New Caledonia, with 17,500 m. tons in 1940, almost twice the 1939 figure. The chief ore is pendlantite, a complex sulfide of iron, copper and nickel found in the Sudbury district, its nickel content is 3 to 3.5 per cent. Monel metal is discussed in Chapter 45.

The deposits in New Caledonia in the South Pacific, the main source of nickel until the Sudbury basin was discovered, consist of an oxidized ore of the garnierite type.

At Copper Cliff (Sudbury) the mixed sulfides are ground fine, classified, roasted in Herreshoff burners to remove some of the sulfur, smelted in reverberatory furnaces and blown in Bessemers with addition of silica-bearing fluxes to remove most of the iron as a slag. The still impure mixed copper and nickel sulfide is then treated by a special process (Orford) in order to concentrate each. It is heated in a reverberatory furnace with sodium sulfate and some coal, so that sodium sulfide results. An essentially

¹⁶ In 1935, 29,880 tons of nickel metal were imported, mainly from Canada.

homogeneous melt results, which is run into medium-sized receptacles and allowed to cool slowly. There is formed at the bottom a hemispherical cake of nickel sulfide with still some copper sulfide, over it, a "tops" of copper sulfide with still some nickel sulfide, and throughout both, sodium sulfide. The bottoms are concentrated further by a second melting, and perhaps a third; similarly the tops. The separation is a physical process; the sodium sulfide serves as floating agent.

The bottoms with 74 per cent Ni and 1.5 per cent Cu are sent to Port Colborne, where they pass successively through a jaw crusher, a ball mill, a 10-mesh screen, to reach a rectangular lead lined tank with false bottom. In this tank, the ground material is leached with hot water to remove sodium sulfide, then, with sulfuric acid to remove most of the remaining iron. The nickel sulfide, now with 76 per cent Ni and 24 per cent S, is divided, and treated further in two ways. One is by roasting on a Dwight-Lloyd sintering machine; the resulting oxide is mixed with 20 per cent coal and heated in an open hearth furnace to give the liquid metal, 96 per cent pure (2 per cent Cu, 1 per cent Fe, S, Co), which is cast, when the furnace is tapped, into thick slabs weighing 490 lbs. These are purified by electrolysis.

The other way is by calcining in a one-hearth calcining oven, with rabbles which stir the ore and also move it at a slow rate toward the hot end, where an oil flame supplies an intense heat, in order to insure the removal of the last of the sulfur. The resulting nickel oxide goes in part to the Mond reducer, a shelf tower with rabbles, where it is reduced to nickel. In part, this metal serves in the purification of the electrolyte liquor, by precipitating an equivalent amount of copper. The black oxide is sold to a considerable extent to potteries for decorating tableware.

The Mond reducer works at 400° F. (204° C.), is 35 feet high and is built of cast iron sections, each having a heating chamber, surmounted by two shelves, one with central, the other with circumferential discharge. A central vertical shaft carries the arms and rabbles. The oxide moves down, as water gas passes upward; from the top, the not quite exhausted water gas is led back, and is burned to furnish the heat (supplemented if needed) to the heating chambers.

For the purification, the anode is suspended in a solution of nickel sulfate, and the metal driven across to the nickel starting sheet (28" × 36"), itself produced by depositing the nickel for 3 days, from the same bath, on aluminum, then stripping off the thin nickel sheet. The anode cycle is 4 days. The electrolytic tanks are concrete, 5' 2" deep, coated with monite, with divisions accommodating 31 anodes and 30 starting sheets, each anode facing a starting sheet less than 2" away. The voltage is 2½ volts; the current density 12 amperes per square foot. As the nickel anode dissolves, copper and iron enter the electrolyte; they are prevented from coming out by the continuous removal of the electrolyte to a purification system and the continuous infeed of purified electrolyte into a canvas box closing the cathode so that an electrostatic head can be maintained which prevents the foul solution from reaching the plate. The precious metals, on the other hand, remain as a mud on the last thickness of the anode;

they are collected, treated as nickel anodes again, for concentration, this time with bags around the anode. The anode mud is then collected and sent to Acton, England, for the recovery of Pt, Pd, Rh, Ru; there is no gold nor silver.

The purification of the nickel sulfate electrolyte is by treatment in Pachuca^{16a} tanks with nickel powder to precipitate copper, a Dorr thickener to remove remaining solids; oxidizers, followed by addition of nickel carbonate, to precipitate iron, and make good the resulting drop in p_H (rise in acidity); the electrolyte is kept at a p_H of 5.2. The liquor is filter-pressed, and is then ready to be fed back to the plating tanks. The capacity of the plant is 420,000 lbs. of 99.95 per cent nickel per day.

In the Mond recovery process, in operation in England, nickel in the metallic form is volatilized by means of carbon monoxide at 100°C . (212°F .) forming the gaseous $\text{Ni}(\text{CO})_4$. Heated to 180°C . (356°F), nickel carbonyl decomposes, leaving the metal behind; the monoxide may be used over again. The deposition is done in small towers, and on nickel shot from previous runs, which are screened to remove the larger sizes. The smaller sizes receive the new deposits, and acquire a structure very much like that of an onion. Before passing through the volatilizing tower, the ore goes through the reducing tower, similar to the system at Port Colborne, just described. The same ore passes reducing tower and volatilizing tower several times.

Over the year, 1940, nickel was quoted at 35 cents a pound.

CHROMIUM

While fuel-fired furnaces have in the past produced an iron alloy with a maximum of 3 per cent chromium, the electric furnace produces alloys of any chromium content, even 99 per cent chromium. The uses for chrome steels and the importance of chrome plating have been discussed (Chapters 45 and 48). Nichrome is a nickel-chrome alloy, with high resistance to the electric current. Stellite contains chromium, cobalt (75 per cent) and tungsten; it is used for high-speed cutting tools, for gears, valves, lathe centers, etc. It is non-magnetic.

The chief ore is chromite $\text{FeO} \cdot \text{Cr}_2\text{O}_3$, with a content of 48 or 45 per cent Cr_2O_3 in the higher grades. The consumption in the U. S. in 1940 was 600,000 long tons of chromite. All but two thousand tons or so, which come from California, must be imported. The main producers are Turkey with 163,646 metric tons, New Caledonia with 55,790 m. tons, Cuba with 52,789 m. tons (1940); Yugoslavia produced 59,527 m. tons, Greece 57,091 m. tons, and the Philippine Islands 126,749 m. tons in 1939. Price \$28 to \$30 a ton.

COLUMBIUM

In the treatment of stainless steels by columbium addition, in order to preserve their corrosion resistance even when heated, and to improve their

^{16a} A Pachuca tank is a tall tank 30 feet to 40 feet high, 14 feet in diameter, with a conical bottom, generally built of wood. A hollow column is set upright in the center of the tank. A stream of compressed air is fed in at the base of the column, driving the "pulp" or slurry upward, and causing it to descend in the wider part of the tank. The air circulation may be supplemented by a stirrer or a pump, or both.

suitability to welding, large quantities of the metal became necessary. Until recently, the stock of columbium consisted of museum samples. Since 1936 it is obtained in fairly large tonnage from African columbite,^{16b} a deposit low in tantalum. A preliminary selective reduction is followed by chloridizing, in order to combine with tin, whose chloride then passes out by volatilization. The residue is reduced with aluminum, or silicon, in an electric furnace, with the production of a ferro-columbium containing 55 per cent Cb, suited to steel making. The production per annum is estimated at close to 500,000 pounds of columbium; all of it produced and consumed in the United States.

Molybdenum is a metal of which the United States has an ample supply. The main producing mine is at Climax, Colorado, and the production in July, 1941, was at the rate of 15,000 tons of ore a day. The ore is concentrated by flotation to 90 per cent MoS_2 . Molybdenum in high-speed tool steels has been mentioned; it is prized as an alloying metal in many steels of the machine and tool grade.

ADDITIONAL PROPERTIES AND USES OF THE METALS; ALLOYS

The main use of copper is for electric motor and generator construction and for transmission lines, as stated in the introduction; it is also used for roofs, flashings, gutters, and conductor pipes; a copper roof coats itself with a layer of green carbonate and oxide which prevents further action. Lead when freshly scratched has a bright surface, which, however, tarnishes within a few minutes; lead is soft, and as such is used in the chemical industries¹⁷ and for covering electrical cables placed underground and undersea. Lead is hardened by adding 1 to 10 per cent antimony. Lead and zinc for storage batteries and dry cells respectively have been mentioned. Both of these metals are made into pigments, and the interesting suggestion has been made, now that titanium pigments are available, that the lead be reserved for storage battery work, letting the titanium pigment replace white lead.¹⁸ Lead wire is used for electrical fuses. A considerable use for zinc is in galvanizing; in wartime, the supply must be conserved for

TABLE 105.—*Properties of metals. Price in cents per pound.*

	1929	1932	1935	1940	Color	Specific Gravity	Melting Point ° F.	° C.	Electrical Conductivity
Copper	18.23	5.67	8.76	11.3	red	8.9	1891 or 1083		100
Lead	6.3	3.0	4.0	5.0	white	11.4	621 or 327		8
Zinc	6.49	2.88	4.33	6.3	white	7.2	786 or 419		27
Tin	45.19	39.12	50.39	49.82	white	7.3	450 or 232		12
Mercury ...	160.7	96	233	white	13.6	liquid		2

or military needs. Tin plating is less important now than formerly. Lead (60 parts) and tin (40 parts) form the valuable and much-used solder. Nickel is electroplated on iron, or better, on iron previously plated with copper; the nickel coat has no luster until the article is buffed. A few comments concerning metals are condensed in Table 105.

^{16b} "Columbium, from a laboratory curiosity to a widely used commercial product." James H. Bennett. *Trans. Electrochem. Soc.*, 69, 63 (1936). See Chapter 48.

¹⁷ Chapter 45.

¹⁸ Chapter 31.

The price of copper has been held at 12 cents a pound on order of the Office of Price Administration, since September, 1940; lead at 5.85 cents a pound since March, 1941; zinc at 8.25 cents a pound since October 1, 1941. After March 30th, 1942, the use of lead in making tinfoil for wrapping cigarettes and cigars is prohibited, on order of the O P A. The tinfoil industry normally uses about 6000 tons of lead monthly.

In 1916, copper reached 37 cents; production was 963,925 tons contrasted to 575,069 tons in 1914. The price was fixed at 23 cents. Lead and zinc moved with copper; lead sold at 12.25 cents at New York; zinc at 27.5 cents. The average for 1918 was 7.46 for lead, 8.31 for zinc.

The alloys are very numerous, even of the type containing two metals only, for the proportions affect the properties materially; thus for brasses, which consist of copper and zinc, the color is affected, as well as strength, ductility, hardness, and malleability. Bronze is copper and tin, with perhaps a small amount of zinc. Bearing metal, such as Babbitt, contains tin, 89 per cent; antimony, 7 per cent; copper, 4 per cent (for Babbitt No. 1). There are other bearing metals in which copper is the main constituent, and still others which contain much lead; for example, Frary metal, 98 per cent Pb and 2 per cent Ba. Type metal must expand on cooling, so that the letters will be sharp; an example is the composition: lead, 80 per cent; antimony, 20 per cent. Fusible alloys for fire extinguishers (automatic) contain tin, lead, bismuth, and either cadmium or antimony. Brasses are yellow to red; bronzes are brown; all the other alloys given above are white.

OTHER PATENTS

U. S. Patent 2,062,869, conducting chemical and metallurgical operations in a rotary furnace; 1,849,293 and 1,965,251; improvement to the indium plating bath; Canadian Patent 315,060, process of recovering nickel, Robert P. Stanley, assigned to the International Nickel Company, 18 claims.

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For many centuries, gold has been a synonym for wealth; to find gold, man will undergo untold hardships and risk his life, as demonstrated in the gold rush to California in 1849, through the desert; and again in the Klondike gold rush of 1896. In numerous mining and smelting processes, on the other hand, it is a by-product operation, without excitement; the gold is just a by-product of copper. Gold is a unique commodity in that its price does not fluctuate with supply and demand, but is fixed by law. The former figure of \$20.6718 per fine ounce was changed through decrees and legislation between August 9, 1933, and January 31, 1934, to \$35.00. In terms of gold, the dollar is cheaper.

Chapter 50

Gold, Silver, Platinum, Radium, Thorium, and Cerium

The unit in which prices for metals are quoted varies; pig iron is quoted by the ton; copper by the pound; but the precious metals are so valuable that they are quoted by the ounce. Gold has a fixed price,¹ \$35.00 a troy ounce (31.10 grams), the figure which superseded the previous one of \$20.67, in 1934. Silver formerly varied in price, but of late the price has been stabilized¹ by the Government at 71.11 cents a troy ounce, and this was the average figure over the year 1940. For comparison, the 1930 open market figure was 38.47 cents a troy ounce. Platinum is in the neighborhood of \$40 an ounce, while palladium brings \$24. Osmium, iridium, and rhodium are also precious metals; iridium fluctuated between \$125 and \$275 in 1940; in early 1941, the figure of \$175 seemed set. In a general way, the price reflects the scarcity of the metal; the scarcer the metal, the higher the price. The low price of iron reflects its abundance.

Radium belongs to the precious metals as far as price goes, but it is not prepared in the metallic form; it enters the market in the form of radium bromide, RaBr_2 . It occurs in such small quantities and the extraction process is so long, that it is quoted in gram lots, in the neighborhood of 30,000 per gram. The total amount of radium in the world in the form of marketable salts is estimated at not over one pound (1941).

The precious metal scrap is saved with great care and brings high prices; it is reworked into pure metals and useful shapes; as a result more finished metal is refined than the amount of ore mined would indicate.

Thorium and cerium are "rare earth" metals; they enter the market as alloyed metals in pyrophoric (fire-producing) alloys, or as oxides, such as in Welsbach mantles.

Gold and the platinum metals are found mainly in the free or metallic state (native metal); silver occurs partly native, partly as sulfide and other compounds. Native gold is rarely free from silver. In addition to deposits worked solely for their precious metals, there are many copper and lead ores which contain silver and gold, and these "values" are isolated in the process of refining.

¹ Gold Reserve Act, January 31, 1934. For silver, the Act of Congress of July 6, 1939.

GOLD

Gold deposits worked primarily for their gold content occur in many parts of the world, as indicated by Table 106:

TABLE 106.—*World production of gold by countries, in fine ounces.**

	1940
Union of South Africa	14,047,000
Canada	5,322,857
Continental United States	4,862,979
Western Australia	1,191,481
Philippine Islands	1,099,058
Gold Coast	886,000
Mexico	883,117
Southern Rhodesia	826,485
Colombia	631,900
Chile	341,000
Brazil	318,935
British India	289,000
Peru	288,167
New Guinea, Oceania	275,000
Sweden	197,995
New Zealand	179,000
Nicaragua	164,355
Venezuela	146,792
Total	41,560,000

In 1939, there were reported for Chosen 975,000 ounces; Japan, 836,000; Belgian Congo 494,642; Tanganyika 150,000. There are many other smaller producers.

* (Minerals Yearbook.)

Within the United States and territories, the distribution is shown in Table 107:

TABLE 107.—*Mine production of gold in continental United States, by states, in fine ounces.**

	1940
California	1,455,671
Alaska	755,970
South Dakota	586,662
Nevada	383,933
Colorado	367,336
Utah	355,494
Arizona	294,807
Montana	272,602
Idaho	146,480
Oregon	113,402
Total	4,869,949

* Minerals Yearbook.

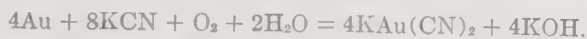
Gold occurs native in two kinds of deposits: hard ores which must be crushed to free the granules of gold, and aluvial gravel which may be dredged. The hard ores are generally "free-milling ores," that is, on crushing them under the hammers (stamps), the gold is freed enough to be extracted by amalgamation or by cyanide solution. The hard ores include the auriferous iron pyrite, in which the gold is in the free state, and may be extracted by the cyanide solutions, without preliminary roasting, but not by mercury. In combined form the chief ore is the telluride. The second

form in which gold-bearing material occurs is as alluvial deposits, chiefly gravels found in the beds of certain present rivers and of rivers of prehistoric times. Within the United States, about as much gold is obtained from lodes (that is, hard rocks) as from gravel. The gravel deposits are called placers, and may be mined for less money than the hard rocks, for the gravel does not require crushing.

Gold nuggets of various sizes have been found in several parts of the world, the largest containing 2284 ounces of gold (Victoria field, Australia), and give the impression that gold-bearing material is rich, but the opposite is true. Nuggets are exceptional, and rich veins of gold are rare; the amount of gold in the ores is generally extremely low. Hard rocks with 1 part of gold to 70,000 parts of worthless gangue are common, while ores with 1 part in 300,000² may still be worked at a profit. For placer deposits, the amount of gold may be still lower and still permit profitable operation.

Gold-bearing Quartz and Other Hard Rocks. Gold-bearing rocks are usually discovered by an outcrop, which soon leads into the ground so that shafts must be constructed and the ore lifted to the surface. It is crushed in a gyratory³ and jaw crushers,³ or stamps, of which the latter are the older practice. A stamp battery consists of 5 hammers (stamps) with long stems; they are lifted by a cam, and drop by gravity onto the ore resting in a steel die at the bottom of a cast-iron crucible which accommodates the dies. Water enters from one side and leaves carrying the crushed rock on the other. The slurry may be worked for its gold in several ways; it is allowed to flow over slightly inclined amalgamated copper plates, which retain the gold, allowing the gangue, but also the auriferous pyrite, to pass. The discharge from the plates is then extracted with cyanide solution. Or, mercury may be added to the stamp crucible (direct amalgamation). The amalgam from the plates (scraped off) or from the stamps is pressed in soft leather or flannel bags to remove the liquid mercury, and the remaining amalgam is retorted. The product from gyratory and jaw crushers is treated similarly. Not infrequently, the crushed material is first concentrated on a shaking, inclined table over which water flows, carrying off the lighter gangue; the concentrates only are passed over the amalgamated plates.

Cyanide Process. The tailings from the amalgamated plates still contain some gold, which may be recovered by treating them with a cold (sodium or potassium) cyanide solution in the presence of air. It is becoming the custom to dispense with the amalgam method of recovery and treat the crushed ore directly with the cyanide solution. The ore is first reduced to fine powder in a ball mill, and the product is then agitated, cold, in a series of tanks, with a dilute cyanide solution:

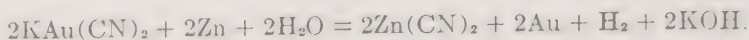


The cyanide method has among other advantages this one, mentioned before, that gold accompanied by pyrite may be extracted without roasting, or fine grinding.

¹ The Santa Barbara mines at Lead and Deadwood recover gold worth \$3.50 per ton of rock; the one mine at Porcupine (Ontario) recovers gold worth \$7.50 per ton (based on \$20.67 an ounce).

² Chapter 44.

The cyanide slurry is filter-pressed; the filtrate contains the gold. In order to isolate it, metallic zinc in the form of shavings is added; the gold powder with excess zinc is treated with sulfuric acid, which removes the zinc and leaves the gold. The latter is then melted with fluxes in a furnace and refined in any one of various ways. The precipitating reaction may be represented as follows:



At some mines, the cyanide solution is passed into a pebble mill of the continuous type (Hardinge⁴) so that dissolving and pulverizing go on at the same time.

The cyanide solution leaving the zinc-gold is brought up to the standard strength, and is used over again.

Gold Telluride. Tellurides of gold are widely distributed, occurring for example at Cripple Creek, Colorado, in Calaveras County, California, and in western Australia. Calaverite is a bronze-yellow ore, AuTe_2 , with a small amount of silver; 40 per cent Au, 56 per cent Te, 3.5 per cent and less Ag. Silver telluride with some gold (7 per cent or less) also occur. It must be roasted in a furnace in order to remove the tellurium as dioxide, before treating with cyanide.

Placer Mining. Placer mining furnishes about three-fourths of the world's gold; placers are the source of most of the gold in South Africa, Russia, the Klondike, and of part of the gold mined in California. The gold-bearing gravels at the surface of the earth are the result of the weathering and erosion of gold originally deposited in hard rock as lodes. It is reasonable therefore to look for a lode near-by when a gold-bearing gravel has been located; in many cases, the lode has been discovered. The large-scale method of operation is by dredging, washing the gravel on the boat, discharging the waste stones, and concentrating the gold from the sand on shaking tables. The dredge brings up the gravel by means of steel buckets on an endless chain; it is dumped into a trommel and rotated there while water is played on it; the sand passes through the perforations in the trommel and drops onto the shaking tables (also called classifiers) and concentrated there. The concentrates are carried to the extraction plant. Care is taken to dump the waste in one direction while the dredge moves forward in the other, so that no gravel will be reworked. One or two men operate the dredge.

Dredging is done not only on rivers which have a flow of water, but also in dry territory, provided water may be sent in by pipes from a river or lake not too far distant. A pit is dug, large enough to accommodate the dredge, and enough water pumped in to float it; operations then proceed as they would in a river.

Dredging is an extension of the hand operation called panning, still employed by prospectors and by individual operators without other equipment. The pan is a circular dish with a small pocket in the bottom; it is filled with gravel, and held under a gentle stream of water; on rotating it.

⁴ Chapter 44.

the lighter parts are gradually floated off, and the gold particles are found in the pocket.

Hydraulic Mining. Another extension of panning is hydraulic mining, in which powerful streams of water discharged through nozzles as large as 11 inches in diameter are played in a solid column against the side of a hill whose gravel is gold-bearing. The gravel is floated along gullies to a sluiceway, an inclined plank floor with cross-pieces, against which the gold particles lodge. Once a week, or more often, the water is turned off and a "clean-up" performed; the cross-pieces are removed and the gold collected. Mercury may be added to the sluice box; it will lodge against the "riffles" also and retain the gold.

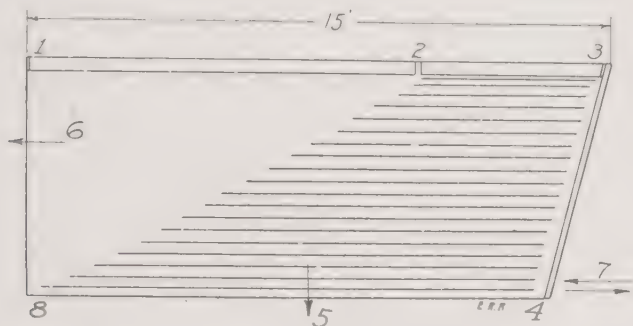


FIGURE 288b.—Principle of a shaking table (Wilfley). Water enters from trough 1-2; slurry from 2-3; the table moves as shown by 7; 1-8 is several inches higher than 3-4, so that the concentrates move uphill and are discharged at 6; the gangue goes off at 5. The table is covered with linoleum, on which the riffles are tacked as shown. Moving mechanism not drawn.

Gold is rarely free from silver; placer gold is generally purer than lode gold.

Gold may also be removed from crushed rock or gravel by chlorination.

Purification of Gold. The native metal or metal recovered from scrap may be purified from base metals such as lead by the furnace process called **cupellation** and described under **silver**.

In order to remove any silver in the gold, either a sulfuric or nitric acid treatment is performed, or an electrolytic method, that of Moebius, is employed. In the acid method, the silver is dissolved and leaves the gold behind, but the protective action of the gold is so great that unless the silver present amounts to 80 per cent, the acid has no effect. Gold which contains less silver must first be melted with an extra amount before the separation from the silver, called the "parting," is effected.

The electrolytic method is the one usually employed in the United States. The anodes are doré silver, that is, gold-bearing silver; the cathode is a movable silver belt with a light coating of oil. The belt moves in a trough of redwood coated with an acid-resisting paint. The bath is silver nitrate, kept slightly acid with nitric acid. The belt moves under the cathodes and

is brushed off automatically at the turn, delivering silver powder. Each anode is hung in a fabric basket in which the gold slime deposits. The slimes are collected at intervals, washed with sulfuric acid, and melted for gold metal.

Properties and Uses of Gold. The pure metal may be hammered so thin that 250,000 sheets are required to make up 1 inch in thickness; the sheets are used for lettering book bindings. For coinage, gold is alloyed with copper, which hardens it; the pure metal is too soft for coinage purposes. The United States coinage is 900 fine^a (900 parts gold and 100 parts copper). For jewelry, alloys with various proportions of gold are used, expressed in terms of carats; pure gold is 24 carat, 18 carat gold is 75 per cent gold. In dental work, gold is of great value, for it is unattacked by saliva or foods.

Gold is permanent in the air; it is unattacked by acids (except aqua regia and selenic acid); its characteristic yellow color is redder in copper alloys, greener in silver alloys. White gold is the palladium alloy.

SILVER

Silver is found alloyed with gold, and to a minor degree, as metallic silver enclosed in silver ores; the more general occurrence is in the form of compounds, and of these the sulfide of silver, argentite, is the principal ore. As stated under gold, much silver is recovered from copper and lead ore, during the refining process. It is interesting to note that in several localities in which gold, silver, and copper have been mined, the gold is above the silver, and the silver above the copper, so that a mine started as a gold mine became a silver mine and later a copper mine as the depth of the shaft increased (Old Dominion Copper Company, Arizona). As with gold, much of the refined silver has its origin in silver scrap. The countries which produce the bulk of the new silver are indicated in Table 108.

TABLE 108.—*World production of silver, in fine ounces in 1940 and other years as stated.**

Mexico	82,640,074
United States	68,286,535
Canada	23,815,715
Japan (1938)	10,100,000
Peru	18,450,250
New South Wales	9,500,000
U. S. S. R. (1938)	8,022,000
Germany and Austria (1938)	7,010,000
Burma (1939)	6,175,000
Bolivia	5,626,380
Honduras	3,892,770
Queensland	3,885,962
Argentina	3,242,200
Chosen (1937)	2,672,978
Yugoslavia (1939)	2,293,634
Belgian Congo (1939)	2,085,000
Chile	1,515,563
Newfoundland	1,494,066
Total	275,654,000

* Minerals Yearbook.

^a No longer binding by law; since April, 1933, the United States "have been off the gold standard," that is, the gold coin may be minted as low as 450 fine, at the discretion of the President.

It will be noted that the Transvaal, which leads in gold production, does not appear in the table; its silver production is only 1,047,000 ounces (1935). On the other hand Mexico, which is sixth in gold production, leads all other countries in silver produced. The production of Bolivia is slightly less than that of Germany, while that of Peru is five times greater than that of Spain. It will also be noted that the world's production of silver is much greater than that of gold. Within the United States and territories, the main producers are shown in Table 109.

TABLE 109. *Mine production of silver for 1936 in the United States in fine ounces.**

Idaho	17,552,240
Montana	12,361,050
Utah	12,172,299
Colorado	9,710,709
Arizona	7,075,215
Nevada	5,175,928
California	2,359,776
New Mexico	1,407,839
Texas	1,326,150
Total	70,092,800
Philippine Islands	1,275,384 not included

* Minerals Yearbook.

In Guanajuato, the ore is of the free-milling type, with the metal in the native state; this district is losing in importance, while a new Mexican center, Parral, in Chihuahua, is gaining.

For the sulfide ore, argentite, the process consists of a roasting on the hearth of a reverberatory furnace, followed by addition of charcoal and further heating to reduce the oxide to the free metal, which is run off in the molten state.

If the ore is lead-bearing, as it often is, more lead may be added until a free-flowing (easily melted) metal is obtained from the first ore treatment. This lead alloy is put through the process of cupellation which removes the lead in the form of the oxide, PbO , litharge, leaving the silver metal on the hearth.

The cupel might be described as an open-hearth furnace with the hearth of special construction; it is made by ramming bone ash into an iron form; the bone ash is moistened with a potassium carbonate solution. In the center a shallow depression is scooped out. After drying, the cupel bottom is ready for use. Its function aside from furnishing a refractory base of non-contaminating material is to absorb a portion of the fused litharge, litharge solution of base metals, and liquid slags formed by the addition of fluxes. The greater part of the litharge is run off through a gutter and collected; if made from a rich alloy, it may retain some silver and must then be re-treated again in the reverberatory furnace, and cupelled again; if made from a weak alloy, it enters the market, and is used, for instance, for making the brilliant lead-potash glass for tableware. A lead alloy containing 500 ounces to the ton is considered a weak alloy; one containing 4000 ounces to the ton a rich one.

The process requires a blast of air directed onto the metals on the hearth. The end of the operation is reached when the last film of

oxide is removed; the silver flashes out brightly, reflecting the arch of the furnace as a mirror would. The purity of the silver is 99.8 per cent. or 998 fine.

The cupel is used not only for silver but also for other precious metals; a silver-gold alloy is usually the result of cupellation. Bone-ash crucibles may be used as well as a hearth of bone ash.

Silver is prized for its beautiful color; its surface takes a high polish. Its uses depend in part upon its superior color and its stability in the air (jewelry, tableware). Silver coins usually contain 5 to 10 per cent copper.

An important use of silver is in photography,⁶ in the form of silver bromide and chloride, sensitive to light; another commercial use of silver salts (the nitrate) is in making mirrors.⁷

Indium. It was discovered that the addition of indium to silver renders such silver, whether solid silver or plated ware, tarnish-proof.⁸ The indium may be incorporated in the silver by hanging two cathodes, one an indium rod, one a silver rod, in the plating bath, with the two double salts of potassium cyanide and indium and silver, dissolved in the plating bath: the object to be plated forms the cathode. With a density of .07 ampere per square inch, a deposit of 4 to 5 per cent indium is formed. By raising the current density to .1, a deposit with 11 per cent indium is formed. By varying the current density, the proportion of indium may be varied at will. A second method is to deposit alternate layers of silver and indium, and then to heat in an oven in order to allow the metals to diffuse. A bluish color which the indium imparts to silver is counteracted by a further improvement, namely, by depositing a silver-gold alloy^{8a} instead of silver, and alternating with indium. For example, 12½ per cent gold, 87½ per cent silver, alternating with indium, heating first to 110° C. (230° F.) for 8 hours, then to 165° C. (329° F.) for 18 hours. The yellow of the gold neutralizes the blue of the indium. The electrodeposition of indium is facilitated by the addition to the plating bath of an organic compound of an acid nature which has the effect of retaining the indium salt in solution, while without it, it tends to separate from the bath^{8b}; such a compound is glycine. The current density recommended in one example for the glycine-containing bath is .035 ampere per square inch.^{8c}

Indium plated on copper also produces a tarnish-proof surface.^{8d}

PLATINUM

Platinum is a white metal, more resistant to chemical agents than silver but not more beautiful in color. It is much heavier than silver (21.5 against 10.5). The production of platinum is usually less than that of gold. Formerly platinum was considered of no value⁹; with the development of

⁶ Chapter 37.

⁷ Chapter 11.

⁸ Canadian Patent 338,197 and U. S. Patents 1,959,668; 1,847,941.

^{8a} U. S. Patent 1,934,730.

^{8b} U. S. Patent 1,935,630.

^{8c} For the source and extraction of indium, see chapter 49.

^{8d} U. S. Patent 1,960,740.

⁹ In the 18th century, a boat-load of platinum brought to Spain from the new world was ordered sunk as valueless. The earliest record of the incident discovered to date is one in Diderot and d'Alembert's *Encyclopédie ou Dictionnaire raisonné de Sciences*, published 1778; tome XXV, p. 187: "On assure que le roi d'Espagne a fait fermer ses mines (de Santaje et de Popayan) et a fait jeter à la mer une très grande quantité de platines pour prévenir les abus que ses sujets en faisoient."

chemical analysis, it was found that platinum vessels resisted heat and the action of most chemical reagents except aqua regia which dissolves it slowly, and some others.¹⁰ For many years, sulfuric acid made in the lead chambers was concentrated in platinum pans; at the present time, it functions in a new way in the manufacture of the same acid, namely, as a catalyst.¹¹ Platinum is used extensively in jewelry. Among the many other services which this metal renders, its use in pyrometers must not be overlooked.

Platinum occurs nearly altogether as a native metal, alloyed with palladium, iridium, in alluvial deposits chiefly.¹² The principal regions of production are shown in Table 110:

TABLE 110.—*World production of platinum, in troy ounces and other platinum group metals for 1939.*

	(a) Platinum	(b) Other platinum metals	Both (a) and (b)
Canada	148,877	135,402
U. S. S. R. placer platinum	100,000 est.
U. S. placer platinum (1940)	36,500
Union South Africa	59,311
Total for platinum and allied metals for 1939	531,000

In the United States the small amount of primary platinum in former years was a by-product of California placer gold; the increased production is due to workings on Squirrel Creek, Goodnews Bay, Alaska, started in 1935, and expected to yield 10,000 ounces annually. The 1940 production from Goodnews actually was 35,000 ounces.

The Russian production comes from the Ural Mountains, where there are several districts; the most important ones at the present time are those of the two rivers, the Iss and the Wija, which combine to form the Tura. The gravels of the river beds carry the platinum values over a distance of about 90 miles. The recovery is by hand panning, or by placer mining.

The platinum produced in Colombia is mainly a by-product of gold production, by panning or placer mining. Platinum is also recovered in the process of refining copper (Anaconda) and nickel ores.

The Russian crude platinum contains iron; nearly all platinum from placer mining carries iridium, and some also osmium, palladium, and other impurities. Iron is removed by hydrochloric acid. Platinum, palladium, and iridium may be separated by solution in aqua regia and heating the chlorides formed to 125° C.; from the solution of the resulting chlorides, ammonium chloride precipitates the platinum. It is reduced to platinum black, which is fused in the electric furnace or in the hydrogen-oxygen flame to the metal. The platinum prepared in this way retains about 2 per cent iridium, which is desirable, for the iridium hardens it.

The precious metals must be melted in the course of the manufacture of sheets, foils, wires, and shapes of various kinds, in order to form alloys of

¹⁰ Phosphorus, arsenic, and bismuth compounds, alkali cyanides and sulfides, carbon from a smoky fire, attack platinum.

¹¹ Chapter 1.

¹² Alluvial deposits are secondary deposits; the original platinum-bearing rock has weathered and has been moved by water.

suitable compositions, or for remelting the cuttings and end-pieces, or for a purification. This may be done in an induction furnace, rapidly, and without danger of contamination by even gaseous fuel. The induction furnace¹³ consists of a fire-clay crucible, for example, 3 inches in diameter, which is set in a coil of one-fourth inch iron pipe through which cold water circulates, plastered with asbestos mud in which the primary winding is placed. The metal scrap in the crucible is the secondary. A current of 250 volts (15 kilowatts) is transformed to 8000 volts in a transformer with reactance, and delivered to a condenser with a discharge gap; a frequency of 30,000 to 50,000 cycles (per second) is obtained. On connecting the primary, the metal begins to glow in a few seconds, and melts in 2 minutes or so, while the crucible remains cold to the touch. The liquid metal is violently agitated by the induced current.¹⁴ A temperature of about 5500° F. (3038° C.) may be attained. By placing the crucible and furnace under a glass bell-jar and connecting it to a strong suction pump, occluded gas may be completely removed, an important precaution in materials for dental alloys.

The usual method of melting platinum is to place the metal pieces in a cavity in a two-piece block of lime, and to introduce the oxy-hydrogen flame (or the oxygen-gas flame) through an opening in the upper half of the lime block; the necessary high temperature, 3191° F. (1755° C.), the melting point of pure platinum, is thus reached.

In 1940, 122,978 ounces of platinum were sold to consumers (U. S.); 42 per cent to jewelers, 25 per cent to the chemical industries, mainly for contact catalysis, but also for linings, nozzles, thermocouples, and furnace windings; 14 per cent to the electrical industry; 8 per cent to dental industry. Osmium, rhodium and ruthenium are not far from \$50 an ounce.

RADIUM BROMIDE

Radium was originally concentrated from pitchblende, a uranium oxide ore found in Joachimstahl, in the northwestern part of Czechoslovakia. In the United States, it was concentrated in Pittsburgh, from carnotite, a sandstone impregnated with uranium vanadate. Radium is always found associated with uranium ores; it is a disintegration product of uranium. At the present time, the American mines and plants are not operated, because the low-grade American ores cannot compete with the high-grade ore from Canada's Arctic and the Belgian Congo. Since 1923, ore from Katanga has been shipped to Belgium and there treated. Since 1933 the Canadian mines have been producing.

It was only for a short time, however, that the Katanga ore headed the market; it has now been displaced in point of richness by the pitchblende deposits on LaBine Point, named after the discoverer Gilbert LaBine, on the eastern edge of Great Bear Lake, Northwest Territories, Mackenzie District, Canada, and just south of the Arctic Circle. The discovery was in 1930. The main deposit is a vein 1400 feet long which on analysis of official samples was shown to run 62 per cent U_3O_8 . The radium content indicates

¹³ The practice at the Williams Gold Refinery Works, of Buffalo, N. Y.

¹⁴ The order in which the metals melt in the induction furnace is the order of their resistivity; the higher it is, the faster the metal melts.

the richness of the ore: there were required 128 tons of the Colorado carnottite to produce 1 gram of radium; of the Katanga ore, 10 tons for the strongest, with an average of 30 to 40 tons. The Great Bear Lake ore is expected to yield 1 gram of radium from only six and a half tons to 10 tons. Theoretically, a 100 per cent U_3O_8 ore contains 1 gram of radium in 4 tons. The ore is concentrated at the mine, then shipped 1600 miles by water over the company's own boats to Edmonton and thence shipped to Port Hope, Ontario (2200 miles) by rail.



FIGURE 289.—The site of the radium ore deposit and the mining camp, Eldorado Mines, in 1937, seven years after the discovery. Great Bear Lake, Point LaBine, Mackenzie, Canada. (Eldorado Mines, Canada.)

In these sub-Arctic hills, 26 miles from the Arctic Circle, on the shores of Great Bear, the largest freshwater lake lying wholly within the British Empire, the richest known deposit of radium lay concealed for many centuries. In 1930, Gilbert LeBine discovered the pitchblende veins which contain radium and uranium. By 1937, this flourishing mining camp, Eldorado Mines, had grown up on the site.

The method of recovering radium and uranium is to concentrate the ore, roast the crushed concentrate with salt, reduce it, leach it with hot sulfuric acid, and add barium chloride. The radium precipitates with the barium, lead and silver; the uranium is in solution. The precipitate is boiled with soda ash, to form the carbonates; these are filtered, and on treatment with hydrochloric acid, radium and barium dissolve, and are made into the double bromide. Fractional crystallization gives radium bromide with 90 to 95 per cent $RaBr_2$. Radium bromide is a white solid, soluble in water. The uranium solution gives a sodium uranate, or oxides or other salts. Beginning with June 1937, the capacity at Port Hope has been at the rate of 8 grams of radium per month. The total store of radium available for therapy in the world is about 300 grams.

Much of the Canadian ore contains leaf silver; some contains also rhodochrosite, a manganese carbonate; other veins are high in silica and free from carbonates.



FIGURE 290.—Radium-barium bromide crystals forming during cooling in the Monel pail. The last stages of radium refining at the Eldorado Mines' refinery at Port Hope, Ontario, consists of 23 processes of fractional crystallization, based on the method used by Madame Curie. During these operations, the infinitesimal amounts of the rare substance are slowly liberated from the barium which has been added to enable the workers to keep track of the radium. (Eldorado Mines, Canada.)

The original price of \$100,000 a gram was sharply reduced upon the discovery of the Great Bear Lake deposit. The price is now \$25,000 to \$30,000 per gram, depending on the quantity and use. There is as a by-product uranium oxide, which is sold for \$2.50 per pound of U_3O_8 , a price which should allow many new uses now unknown.

For use in therapy, the radium bromide is generally converted to the sulfate, and put up in small lots of capillary glass of gold tubes. Another

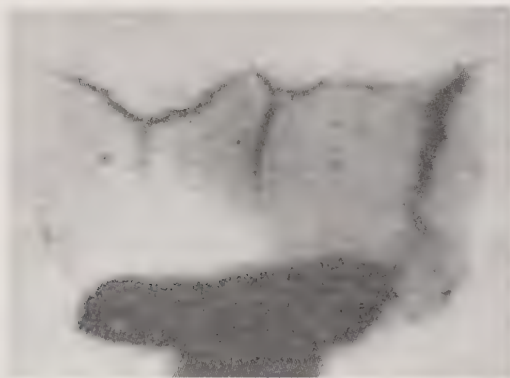


FIGURE 291.—Illustration of industrial gamma-ray radiography. The shadowgraph shows serious defects adjacent to the chipping in a turbine cylinder casting. (Reproduced by permission) (see reading references).

method is to preserve the water solution in a glass system, and pump off every day the gaseous emanation into small glass bulbs, also suitable for the treatment of patients. The standard of strength for either kind is the milli-curie,¹⁵ measured on the gamma-electroscope.

Radium salts are also used in luminous paints mixed with intensifying admixtures such as zinc sulfide or calcium sulfide.

¹⁵ The milli-curie is the radio activity of 1 milligram of radium in equilibrium with its disintegration products. For carnotite treatment, compare *Chem. Met. Eng.*, 11, 586 (1913), also 10, 469 (1912) and 13, 143 (1915). Also "Extraction and recovery of radium, vanadium, and uranium from carnotite," K. B. Thews and F. J. Heinle, *Ind. Eng. Chem.*, 15, 1159 (1923), with flow sheet.

Industrial gamma-ray radiography in the non-destructive testing of metals is a well developed practice. The radium salt (say 200 milligrams of radium) in a pear-shaped container of lead, with windows, is placed at one face of the casting or other piece, a photographic film at the opposite one. The shadowgraph obtained is studied for defects.

THORIUM AND CERIUM

The Welsbach mantle¹⁶ for gas light consists of thoria, ThO_2 , and 1 or 2 per cent ceria, CeO_2 , obtained from monazite sand found in Brazil (the best) and North Carolina and West Virginia. In order to extract thorium and ceria, the sand, washed free from earth, is freed from iron by passing it over electromagnets with low current, from garnet by the same electromagnets



FIGURE 292.—After 93 men in the mines at Great Bear Lake have worked two weeks to produce many tons of ore; after 160 men in the refinery have worked another two weeks, the precious radium material has been reduced to the group of crystals in this single glass flask in the hands of a worker. (Courtesy of the Eldorado Mines, Canada, through Mr. L. E. Westman, Toronto, Canada.)

with high current. The remaining material is treated with sulfuric acid and from this solution the oxalates are precipitated; thorium oxalate is separated by solution in ammonium oxalate, in which cerium oxalate is not soluble. Both are refined further and transformed into the nitrates; these are dissolved and mixed to give the relative amounts corresponding to the figures above. In order to make the mantle, a weave of cotton or rayon is soaked with the solution of the nitrate mixture, dried, and ignited. The resulting shape consists of the oxides; it is dipped in collodium to stiffen for transport. Soft mantles are also made. The Welsbach mantles will probably always remain of great importance for lighting in isolated places, such as lighthouses on the seacoast.

After the thorium salts are removed, and some of the cerium, there is retained as a by-product a mixture of the salts of cerium, lanthanum, praseodymium, yttrium, and samarium. These salts are changed to the chlorides, and placed, gradually, in an iron crucible forming the cathode, in

¹⁶ The Welsbach plant at Camden, N. J.; *Chem. Met. Eng.*, 21, 497 (1919).

which a carbon anode dips. The crucible is heated just at the bottom to fuse the chlorides. There is obtained a button on the bottom of the crucible consisting of cerium with the other metals named as admixtures. The button is alloyed with 30 per cent iron and made into small pieces one-eighth inch in diameter and 1 inch long, mounted for cigar-lighters. When scratched with a piece of iron, sparks are produced; this is the pyrophoric alloy.¹⁷



FIGURE 293.—Until a few years ago, all the vanadium ore from the Minas Ragva was transported on the backs of llamas to the nearest shipping point. (Courtesy of Dr. B. D. Saklatwalla, of the Vanadium Corporation of America.)

Metallic thorium has been prepared, although not on an industrial scale; a very complete reference is given below.¹⁸

Tungsten in the United States is obtained chiefly from wolframite, a tungstate of iron and manganese found in Colorado.^{18a} Ferrotungstate is manufactured, but also the metal, by forming the tungstic acid, calcining, and reducing with carbon. Tungsten filaments may be made from the metal mixed with sugar, and drawn into a wire which is then heated in an atmosphere of hydrogen; they may also be made by the substitution process, in which a carbon filament is heated in an atmosphere of tungsten oxychloride mixed with hydrogen.¹⁹ Tungsten is required for making the carbide, which is used as a cutting tool, for sand blast nozzles, and wire drawing dies. Tungsten steel for cutting tools has been mentioned in Chapter 48.

¹⁷ U. S. Patent 1,273,223; compare also *Ind. Eng. Chem.*, 10, 849 (1918).

¹⁸ "Metallic thorium," J. W. Marden and H. C. Reutsehler, *Ind. Eng. Chem.*, 19, 97 (1927).

^{18a} The main producers for the world in the order of their importance are: Kiangsi province, China; Burma, United States, Malay States, Portugal.

¹⁹ "Tungsten refining in Europe," C. Matignon, *Chem. Met. Eng.*, 23, 697 (1920).

Steel, brass, nickel, or silver articles may be tungsten plated in an alkaline solution containing dissolved tungstic oxide (WO_3) with 1 per cent of its weight of nickel in solution.²⁰ Without the nickel, the deposition of tungsten stops after a very thin layer has formed, through self-polarization. The article to be plated is made the cathode, while the anode may be platinum.

Vanadium, in the form of ferro-vanadium, finds its chief industrial use in the manufacture of special steels for automotive and other purposes to which it confers unusual strength and resistance to fatigue. The main ores are the patronite, a sulfide of vanadium found in Peru not far from the Cerro de Pasco copper deposits, and carnotite in Colorado. It has been shown that chemically vanadium resembles tantalum, and not antimony and bismuth.²¹

OTHER PATENT

U. S. Patent 2,029,387, agent to improve the metal deposit from a plating bath.

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²⁰ U. S. Patents 1,885,702; 1,885,701; 1,883,235.

²¹ *Ind. Eng. Chem.*, **19**, 787 (1927), J. W. Marden and M. N. Rich.

Appendix

Table of the More Important Chemical Elements with Their Symbols and Atomic Weights

(From the International Table of Atomic Weights for 1941)

Aluminum	Al	26.97	Manganese	Mn	54.93
Antimony	Sb	121.76	Mercury	Hg	200.61
Argon	A	39.944	Molybdenum	Mo	95.95
Arsenic	As	74.91	Neon	Ne	20.183
Barium	Ba	137.36	Nickel	Ni	58.69
Beryllium	Be	9.02	Nitrogen	N	14.008
Bismuth	Bi	209.0	Osmium	Os	190.2
Boron	B	10.82	Oxygen	O	16.000
Bromine	Br	79.916	Palladium	Pd	106.7
Cadmium	Cd	112.41	Phosphorus	P	30.98
Calcium	Ca	40.08	Platinum	Pt	195.23
Carbon	C	12.01	Potassium	K	39.096
Cerium	Ce	140.13	Radium	Ra	226.05
Cesium	Cs	132.91	Radon	Rn	222.
Chlorine	Cl	35.457	Rhodium	Rh	102.91
Chromium	Cr	52.01	Rubidium	Rb	85.48
Cobalt	Co	58.94	Selenium	Se	78.96
Columbium	Cb	92.91	Silicon	Si	28.06
Copper	Cu	63.57	Silver	Ag	107.88
Fluorine	F	19.0	Sodium	Na	22.990
Gold	Au	197.2	Strontium	Sr	87.637
Helium	He	4.003	Sulfur	S	32.06
Hydrogen	H	1.008	Tellurium	Te	127.61
Iodine	I	126.92	Thorium	Th	232.12
Iridium	Ir	193.1	Tin	Sn	118.70
Iron	Fe	55.85	Titanium	Ti	47.90
Krypton	Kr	83.7	Tungsten	W	183.92
Lanthanum	La	138.92	Uranium	U	full val 238.07 _e
Lead	Pb	207.21	Vanadium	V	50.95
Lithium	Li	6.940	Zinc	Zn	65.38
Magnesium	Mg	24.32	Zirconium	Zr	91.22

Table for Conversions

1 meter = 39.37 inches	1 square meter = 10.7631 square feet
1 foot = 304.80 millimeters	1 ounce avoirdupois = 28.35 grams.
1 inch = 25.40 millimeters	1 ounce troy = 31.10 grams.
1 pound = 453.6 grams	
1 cubic foot = 28.315 liters; 1 cubic foot of water at 62° F. weighs 62.321 pounds.	
1 cubic foot contains 7.48 gallons (U. S.); 1 cubic meter = 35.3166 cu. ft.	
1 gallon (U. S.) of water weighs 8.33 pounds.	1 gram mole of a gas at S.T.P.
1 gallon (English) of water weighs 10.0 pounds.	= 22.4 liters = 0.791 cubic foot.
1 kilometer = 0.6214 mile.	1 μ = 10^{-6} meter = 10^{-4} centimeter
1 gross ton = 1 long ton = 2200 pounds.	= 10^{-3} millimeter
1 short ton = 1 net ton = 2000 pounds.	1 $m\mu$ = 10^{-6} millimeter = 10 A.U.
1 metric ton = 1000 kilograms = 2205 pounds.	

To change centigrade degrees to Fahrenheit degrees, multiply by 9/5 and add 32.

The British Thermal Unit (Btu.) is the quantity of heat necessary to raise 1 pound of water 1° F. from 60 to 61°; it also equals 777.52 foot-pounds.

The large Calorie, also called the kilogram calorie (Cal), is the amount of heat necessary to raise 1 kilogram of water 1° C. from 17 to 18°.

1 Cal = 3.968 Btu. 970 Btu. are required to vaporize 1 pound of water at 212° F. to steam at 212° F.

The specific heat of water is 1

1 horsepower = 0.7457 kilowatt.

1 kilowatt = 1.341 horsepower.

Horsepower and kilowatts require a time factor to mean a quantity of power.

1 horsepower-hour = 0.7457 kilowatt-hour.

1 horsepower-second = 550 foot-pounds.

1 pound pressure is equivalent to a column of water 2.304 feet high.

Normal atmospheric pressure at sea level is 14.70 pounds per square inch and supports a column of mercury 29.92 inches high at 15° C., or a column of water 33.93 feet high at 15° C., which is also the maximum lift on the suction side of a pump. 29.92 inches = 760 millimeters.

1 volt times 1 ampere equals 1 watt.

1000 watts equal 1 kilowatt.

1 ampere-second deposits 0.001118 grams of silver.

Note: The pound in this table is the avoirdupois pound in every case. Unless otherwise specified, this is the pound meant in ordinary affairs.

Tables on heat values of fuels and on specific gravities of metals and alloys, will be found in the text.

For calculation of costs, consult:

"The technical organization, its development and administration," John Morris Weiss and Charles Raymond Downs, McGraw-Hill Co., New York, 1914.

The number called p_H is a negative exponent of 10; 10 with that exponent, times 1, gives the amount of hydrogen ions, in grams, in 1 liter of the solution. The range is from 1.0 to 14.0, 7.0 being the neutral point.

A cord of wood is a pile 8 feet long, 4 feet wide, and 4 feet high.

See for General Equivalents for Degrees Baumé for Liquids Heavier than Water

* Temperature 60°/60° F.

One gallon distilled water at 60° F. in air = 8.32823 lbs.

Table adopted by the U. S. Bureau of Standards from the formula:

$$^{\circ} \text{Baumé} = 145 - \frac{145}{\text{Sp. Gr.}_{60^{\circ} \text{ F.}}}$$

Degrees Baumé	Specific Gravity 60°/60° F	Pounds per Gallon	Degrees Baumé	Specific Gravity 60°/60° F	Pounds per Gallon
0.	1.0000	8.328	36.	1.3303	11.079
1.	1.0069	8.385	37.	1.3426	11.181
2.	1.0140	8.445	38.	1.3551	11.285
3.	1.0211	8.504	39.	1.3679	11.392
4.	1.0284	8.565	40.	1.3810	11.501
5.	1.0357	8.625	41.	1.3942	11.611
6.	1.0432	8.688	42.	1.4078	11.724
7.	1.0507	8.750	43.	1.4216	11.839
8.	1.0584	8.814	44.	1.4356	11.956
9.	1.0662	8.879	45.	1.4500	12.076
10.	1.0741	8.945	46.	1.4646	12.197
11.	1.0821	9.012	47.	1.4796	12.322
12.	1.0902	9.079	48.	1.4948	12.449
13.	1.0985	9.148	49.	1.5104	12.579
14.	1.1069	9.218	50.	1.5263	12.711
15.	1.1154	9.289	51.	1.5426	12.849
16.	1.1240	9.361	52.	1.5591	12.984
17.	1.1328	9.434	53.	1.5761	13.126
18.	1.1417	9.508	54.	1.5934	13.270
19.	1.1508	9.584	55.	1.6111	13.417
20.	1.1600	9.660	56.	1.6292	13.568
21.	1.1694	9.739	57.	1.6477	13.722
22.	1.1789	9.818	58.	1.6667	13.880
23.	1.1885	9.898	59.	1.6860	14.041
24.	1.1983	9.979	60.	1.7059	14.207
25.	1.2083	10.063	61.	1.7262	14.376
26.	1.2185	10.148	62.	1.7470	14.549
27.	1.2288	10.233	63.	1.7683	14.727
28.	1.2393	10.321	64.	1.7901	14.908
29.	1.2500	10.410	65.	1.8125	15.095
30.	1.2609	10.501	66.	1.8354	15.285
31.	1.2719	10.592	67.	1.8590	15.482
32.	1.2832	10.686	68.	1.8831	15.683
33.	1.2946	10.781	69.	1.9079	15.889
34.	1.3063	10.879	70.	1.9333	16.101
35.	1.3182	10.978			

All densities taken at 60° F. and referred to distilled water at 60° F. as 1.0000.

*Degrees Baumé with Corresponding Specific Gravity for Liquids
Lighter than Water **

$$^{\circ} \text{Baumé} = \frac{140}{\text{sp. gr. } 60^{\circ}/60^{\circ} \text{ F.}} - 130, \text{ at } 60^{\circ} \text{ F.}$$

Degrees Baumé	Specific Gravity 60°/60° F	Pounds per Gallon	Degrees Baumé	Specific Gravity 60°/60° F	Pounds per Gallon
10.0	1.0000	8.328	55.0	0.7568	6.300
11.0	.9929	8.269	56.0	.7527	6.266
12.0	.9859	8.211	57.0	.7487	6.233
13.0	.9790	8.153	58.0	.7447	6.199
14.0	.9722	8.096	59.0	.7407	6.166
15.0	.9655	8.041	60.0	.7368	6.134
16.0	.9589	7.986	61.0	.7330	6.102
17.0	.9524	7.931	62.0	.7292	6.070
18.0	.9459	7.877	63.0	.7254	6.038
19.0	.9396	7.825	64.0	.7216	6.007
20.0	.9333	7.772	65.0	.7179	5.976
21.0	.9272	7.721	66.0	.7143	5.946
22.0	.9211	7.670	67.0	.7107	5.916
23.0	.9150	7.620	68.0	.7071	5.886
24.0	.9091	7.570	69.0	.7035	5.856
25.0	.9032	7.522	70.0	.7000	5.827
26.0	.8974	7.473	71.0	.6965	5.798
27.0	.8917	7.425	72.0	.6931	5.769
28.0	.8861	7.378	73.0	.6897	5.741
29.0	.8805	7.332	74.0	.6863	5.712
30.0	.8750	7.286	75.0	.6829	5.685
31.0	.8696	7.241	76.0	.6796	5.657
32.0	.8642	7.196	77.0	.6763	5.629
33.0	.8589	7.152	78.0	.6731	5.602
34.0	.8537	7.108	79.0	.6699	5.576
35.0	.8485	7.065	80.0	.6667	5.549
36.0	.8434	7.022	81.0	.6635	5.522
37.0	.8383	6.980	82.0	.6604	5.497
38.0	.8333	6.939	83.0	.6573	5.471
39.0	.8284	6.898	84.0	.6542	5.445
40.0	.8235	6.857	85.0	.6512	5.420
41.0	.8187	6.817	86.0	.6482	5.395
42.0	.8140	6.777	87.0	.6452	5.370
43.0	.8092	6.738	88.0	.6422	5.345
44.0	.8046	6.699	89.0	.6393	5.320
45.0	.8000	6.661	90.0	.6364	5.296
46.0	.7955	6.623	91.0	.6335	5.272
47.0	.7910	6.586	92.0	.6306	5.248
48.0	.7865	6.548	93.0	.6278	5.225
49.0	.7821	6.511	94.0	.6250	5.201
50.0	.7778	6.475	95.0	.6222	5.178
51.0	.7735	6.440	96.0	.6195	5.155
52.0	.7692	6.404	97.0	.6167	5.132
53.0	.7650	6.369	98.0	.6140	5.110
54.0	.7609	6.334	99.0	.6114	5.088
55.00	.7568	6.300	100.0	.6087	5.066

* Bureau of Standards, Circular No. 57.

Degrees A. P. I. American Petroleum Institute) and Corresponding Specific Gravity for Petroleum Oils, Mainly for Liquids Lighter Than Water, at 60° F. Referred to Water at 60° F.*

$$\text{Degree A.P.I.} = \frac{141.5}{\text{sp. gr. } 60^{\circ}/60^{\circ} \text{ F.}} - 131.5$$

Degrees A.P.I.	Specific Gravity 60°/60° F	Pounds per Gallon	Degrees A.P.I.	Specific Gravity 60°/60° F	Pounds per Gallon
10.00	1.0000	8.328			
11.00	.9930	8.270	56.00	.7547	6.238
12.00	.9861	8.212	57.00	.7507	6.249
13.00	.9792	8.155	58.00	.7467	6.216
14.00	.9725	8.099	59.00	.7428	6.184
15.00	.9659	8.044	60.00	.6389	6.151
16.00	.9593	7.989	61.00	.7351	6.119
17.00	.9529	7.935	62.00	.7313	6.087
18.00	.9465	7.882	63.00	.7275	6.056
19.00	.9402	7.830	64.00	.7238	6.025
20.00	.9340	7.778	65.00	.7201	5.994
21.00	.9279	7.727	66.00	.7165	5.964
22.00	.9218	7.676	67.00	.7128	5.934
23.00	.9259	7.627	68.00	.7093	5.904
24.00	.9100	7.578	69.00	.7057	5.874
25.00	.9042	7.529	70.00	.7022	5.845
26.00	.8984	7.481	71.00	.6988	5.817
27.00	.8927	7.434	72.00	.6953	5.788
28.00	.8871	7.387	73.00	.6919	5.759
29.00	.8816	7.341	74.00	.6886	5.731
30.00	.8762	7.296	75.00	.6852	5.703
31.00	.8708	7.251	76.00	.6819	5.676
32.00	.8654	7.206	77.00	.6787	5.649
33.00	.8602	7.163	78.00	.6754	5.622
34.00	.8550	7.119	79.00	.6722	5.595
35.00	.8498	7.076	80.00	.6690	5.568
36.00	.8448	7.034	81.00	.6659	5.542
37.00	.8398	6.993	82.00	.6628	5.516
38.00	.8348	6.951	83.00	.6597	5.491
39.00	.8299	6.910	84.00	.6566	5.465
40.00	.8251	6.870	85.00	.6536	5.440
41.00	.8203	6.830	86.00	.6506	5.415
42.00	.8155	6.790	87.00	.6476	5.390
43.00	.8109	6.752	88.00	.6446	5.365
44.00	.8063	6.713	89.00	.6417	5.341
45.00	.8017	6.675	90.00	.6388	5.316
46.00	.7972	6.637	91.00	.6360	5.293
47.00	.7927	6.600	92.00	.6331	5.269
48.00	.7883	6.563	93.00	.6303	5.246
49.00	.7839	6.526	94.00	.6275	5.222
50.00	.7796	6.490	95.00	.6247	5.199
51.00	.7753	6.455	96.00	.6220	5.176
52.00	.7711	6.420	97.00	.6193	5.154
53.00	.7669	6.385	98.00	.6166	5.131
54.00	.7628	6.350	99.00	.6139	5.109
55.00	.7587	6.316	100.00	.6112	5.086

* Bureau of Standards, Circular C 410.

DIESEL FUEL STANDARDS

The following specifications for Diesel Oils are given because these fuels are comparatively new, and it is difficult to find specifications for them in the usual collections.

Criteria of Diesel Fuels, Their Relative Importance, L. J. Le Mesurier, Anglo-Iranian Oil Co. Petroleum Times 37, 85 (1937), Jan. 16.

Following are three specifications that have been considered by the British Standards Institution:

“Grade A—For automotive or other similar types of engines with small cylinders. Speed above 800 r.p.m. and high standard of performance essential.

“Grade B—For medium speed engines and powers not less than 25 b.h.p. per cylinder. For example, industrial units and main and auxiliary marine engines.

“Grade C—For large slow-running engines where adequate provision is made for heating and cleaning the fuel.

Grade		A	B	C
Flash point.....	Minimum	150° F.	150° F.	150° F.
Aniline point*.....	Minimum	60° C.	45° C.	...
Hard asphalt.....	Maximum	0.01%	2.0%	4.0%
Conradson carbon.....	Maximum	0.2%	4.0%	8.0%
Ash.....	Maximum	0.01%	0.05%	0.10%
Viscosity redwood No. 1 at 100° F.	Maximum	45"	100"	750"
Pour Point.....	Maximum	20° F.
Sulfur content.....	Maximum	1.0%	2.0%	1.0%
Water content.....	Maximum	Not to exceed 0.1%	0.5%	1.0%
Distillation, Vol. to 350° C.....	Minimum	85%
Calorific value, gross.....	Minimum	19,250	18,750	18,250

* Approximate measure of ignition quality pending the development of a standard engine test."

Army Department Specification for Diesel Fuel. Specification No. 7-0-2c
August 1, 1936.

"B. Grade B-1. Fuel oil for Diesel engine shall be furnished in one grade only.

"C. Material and Workmanship, etc. C-1. Diesel fuel oil shall be a petroleum distillate. It shall be free from grit, acid, and fibrous or other foreign matter likely to clog or injure pumps, nozzles, or valves.

"E. Detail Requirements. E-1. Fuel oil for Diesel engines shall conform to the following chemical and physical characteristics:

Test	Test No.		Limit
	F. S. B.	A. S. T. M.	
Flash point, closed cup, °F., minimum.....	110.22	D93-22	150
Pour point, °F., maximum.....	20.14	D97-33	0
Viscosity, SSU, at 100° F.....	30.43	D88-33	35-45
Water and sediment, per cent, maximum.....	300.32	D96-30	0.05
Total sulfur, per cent, maximum.....	520.22	D129-33	1.0
Carbon residue, per cent, maximum.....	500.13	189-30	0.2
Acid, per cent, maximum.....	542.1	0.01
Corrosion at 212° F., copper strip.....	530.31	(a)
10 per cent distillation temperature, °F., maximum.....	100.14	D86-30	675
Diesel index number, minimum.....	(2)45
A.P.I. gravity.....	40.1	D287-33	
Aniline point.....	310.11		

(1) Negative. (2) See F-4.

"F. Methods of Sampling, Inspection, and Tests.

F-1. Sampling.—Samples shall be taken according to the procedure prescribed in Section F of Federal Specification VV-L-791, referred to in Section A.

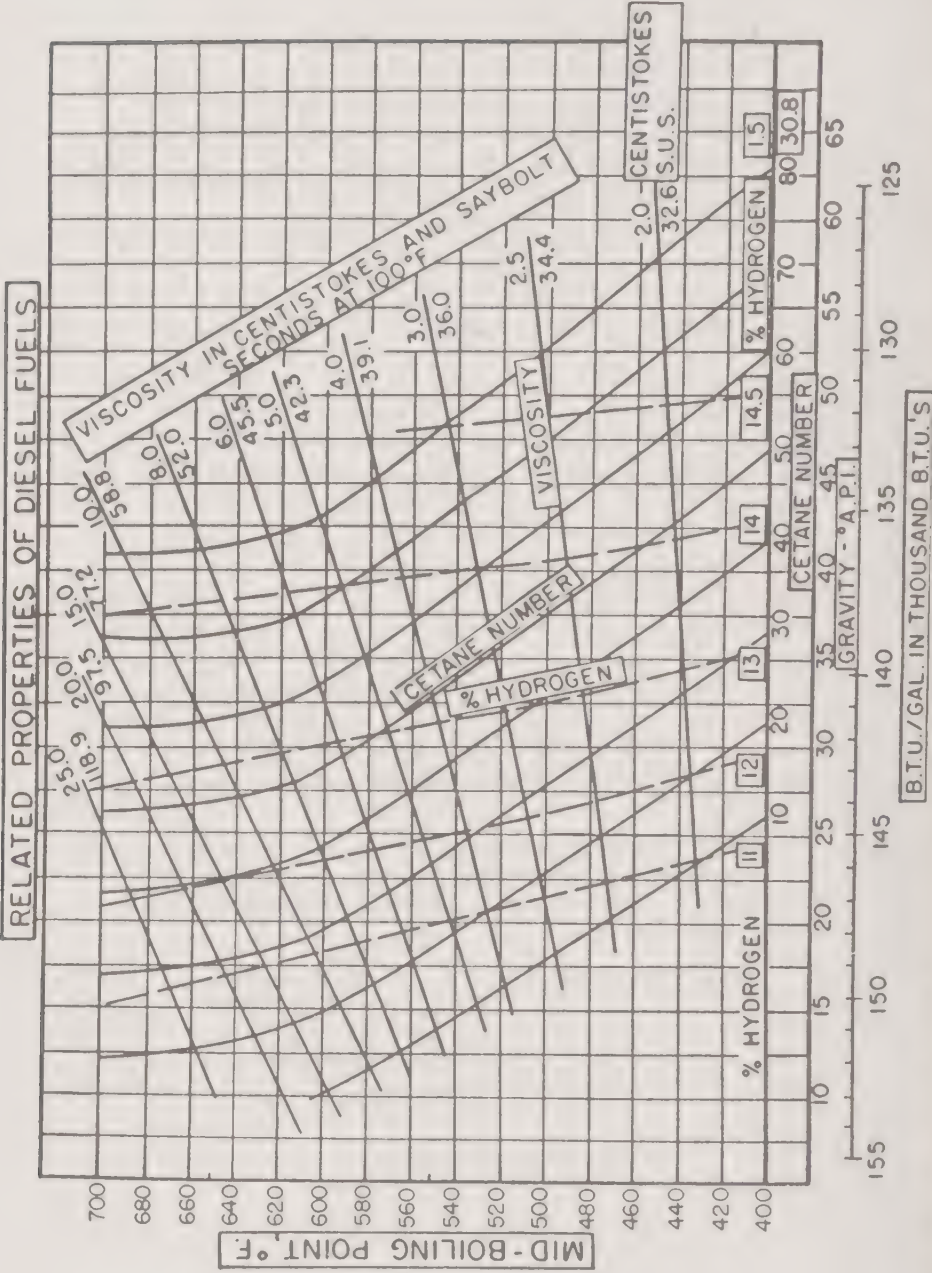
F-2. Inspection and tests.—Unless otherwise specified, all tests shall be made according to the methods for testing contained in section F of Federal Specification VV-L-791.

F-3. Diesel index number.—The Diesel index number shall be determined by the following equation:

$$\text{Diesel index number} = \frac{\text{aniline point (°F.)} \times \text{A.P.I. gravity}}{100}$$

The aniline point shall be determined in °F. by the method described as part method 310.11, Federal Specifications VV-L-791.

F-4. In the event that the fuel supplied fails to exhibit satisfactory ignition quality in use, the right is reserved to require, in lieu of the minimum Diesel index number of 45, a minimum cetane number of 45, as determined in the P.R. turbulent-head type fuel-testing engine by the knockmeter delay method."



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